

CONTROL TECHNIQUES FOR ORGANIC
GAS EMISSIONS FROM FIBERGLASS
IMPREGNATION AND FABRICATION PROCESSES

FINAL REPORT

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ABSTRACT

The objectives of this study were (1) to locate and characterize as many sources of polyester resin/fiberglass process emissions in California as possible; (2) to establish an emission inventory based upon realistic emission factors for the pollutants of interest; and (3) to review the technology for controlling organic vapor emissions from this industry.

We conducted a survey by telephone and by written questionnaire, identifying thereby 305 unsaturated polyester resin users. Between August 1980 and May 1981, the industry used 44.4 to 45.5 million kilograms per year (97.9 to 100.4 million pounds per year) of resin and gel coat; to our knowledge this is the only California-specific estimate based upon an actual survey. The industry was in a recession during this period.

The California polyester resin/fiberglass industry consists of a large number of small firms and a few very large firms. The median firm size is 27,500 kg/yr (60,200 lb/yr) and the range is 99.8 kg/yr (220 lb/yr) to 8.8 million kg/yr (19.3 million lb/yr). The largest 10 percent of the users consume 72 percent of the unsaturated polyester resin. The industry is centered in Los Angeles, Orange and San Diego Counties, which in combination account for 81 percent of the state's resin consumption.

Fabrication processes used in California include hand and spray layup, marble casting, filament winding, bag molding, pultrusion, continuous lamination and matched metal molding. Almost three quarters of the firms in the state use hand layup, spray layup or a combination of the two. Continuous lamination and pultrusion use the most resin per plant. Styrene monomer is used as the cross-linking agent (to polymerize the unsaturated polyester resin) in all but three plants, which use methyl methacrylate. The most common catalysts are methyl ethyl ketone peroxide and benzoyl peroxide.

To develop improved emission factors, we first reviewed published and unpublished data from previous field and laboratory tests. We then conducted source tests at a large continuous lamination plant, a medium-sized spray layup facility, and a large synthetic marble casting plant. The last of these used normal and vapor-suppressed resins on successive days. Total emissions during each test run were determined by integrating the recorder trace of the output of a portable flame ionization detector. The detector was

calibrated by simultaneously collecting organic vapor samples on charcoal traps and analyzing them by gas chromatography. The emission factors developed from the literature review and our tests were based upon styrene or methyl methacrylate monomer input rather than total amount of resin and/or gel coat.

Organic vapor emissions from the industry statewide were estimated to be 1.41 to 2.55 million kg/yr (1549 to 2805 tons/yr). Only 4 percent of the firms account for half of the total emissions. The South Coast Air Basin accounts for 1152 to 2042 tons/yr, or about 73 percent of the statewide total. Emissions from Los Angeles, Orange and San Diego Counties are 262 to 512, 856 to 1478 and 143 to 272 tons/yr, respectively.

Estimated emissions from polyester resin/fiberglass fabrication constitute 0.054 to 0.098 percent of the total organic gas (TOG) emissions, and 0.075 to 0.13 percent of stationary source organic gas emissions, as reported in the 1979 statewide emission inventory. It is difficult, if not impossible, to compare our estimates with those reported in various emission inventories by manufacturing category, since polyester resin/fiberglass operations are often ambiguously or erroneously categorized.

Incineration (at two plants) and use of resins with vapor suppressant additives are the only means of organic vapor emission control in this industry. We reviewed the literature on vapor suppressants and performed laboratory tests on emissions from resin coatings placed in a wind tunnel. Under our test conditions, vapor suppressants indeed reduced weight loss; furthermore, long-term weight loss increased with increasing gel time. To determine whether use of vapor suppressant affected material properties, we performed interlaminar shear strength and bending tests on laminates made of normal and vapor-suppressed resin and glass mat and cloth. Use of vapor suppressant did not degrade the properties measured.

Incineration, activated carbon adsorption, and condensation were found to be applicable in principle to controlling emissions from polyester resin/fiberglass fabrication, although each has some drawbacks. Absorption was not found to be practical. Costs of controlling emissions from hypothetical small and large hand- and spray-layup plants were estimated to be \$10.3 to \$15 per pound of styrene removed for incineration (assuming no heat recuperation), \$4.3 to \$4.6 per pound for carbon adsorption (assuming no credit for

recovered styrene) and \$7.3 to \$15 per pound for condensation (assuming a credit of 60 cents/pound for recovered styrene). These costs are for new installations.

Any control strategy developed for this industry should take into account the heavy concentration of emissions among a relatively small number of firms. Strategies examined included setting maximum emission levels, requiring a minimum percentage removal of organic vapors, and requiring specific control technology.

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- (5) The industry is centered in Los Angeles, Orange and San Diego Counties, which in combination account for 63 percent of the number of firms and 81 percent of the state's resin consumption.
- (6) The next-largest resin-using counties are Santa Clara, Sacramento and Alameda, whose 43 firms account for another 4 percent of the state's resin use.
- (7) Most of the large firms are in Southern California, although the average resin use per firm in Sacramento, San Joaquin and Yolo Counties is actually higher than in Los Angeles and Orange Counties.
- (8) The great majority of the firms and the resin use are centered in the South Coast Air Basin (federal Air Quality Control Region 24).

1.1.3 Use by Product and Production Process

- (1) Our survey identified 17 major types of products made with polyester resin/fiberglass processes in California.
- (2) The 16 firms which manufacture panels and bathroom fixtures use almost 25 million kg/yr (55 million lb/yr) of resin and gel coat, or about 55 percent of the state total.
- (3) While plants which manufacture boats, synthetic marble, and laminates in general comprise over half of the user population, they account for only about one quarter of the total unsaturated polyester resin use.
- (4) Panel and bathroom fixture plants average 2.5 million kg/yr (5.6 million lb/yr) and 550,000 kg/yr (1.2 million lb/yr) per plant, respectively. The smallest operations are the surfboard manufacturers, who average only 6,900 kg/yr (15,000 lb/yr) per firm.
- (5) Fabrication processes used in California include hand and spray layup, marble casting, filament winding, bag molding, pultrusion, continuous lamination and matched metal molding.
- (6) Almost three quarters of the firms in California use hand layup, spray layup or a combination of the two.

1.0

FINDINGS AND CONCLUSIONS

1.1 SURVEY OF POLYESTER RESIN USERS IN CALIFORNIA

1.1.1 Statewide Polyester Resin Use

- (1) Our survey obtained detailed information on 291 polyester resin/fiberglass fabricators and partial information on another 14.
- (2) It is likely that many small firms were not identified; however, their contribution to statewide resin use is believed to be miniscule.
- (3) We estimate that 44.4 to 45.5 million kg/yr (97.9 to 100.4 million lb/yr) of unsaturated polyester resin is used in California. To our knowledge, this is the only California-specific estimate based upon an actual survey.
- (4) During the survey period (August 1980 to May 1981), many firms were operating below their normal capacities. About 15 percent of the firms we contacted had gone out of business. These findings are consistent with the depressed state of this industry nationwide in 1980.

1.1.2 Distribution of Resin Users by Size and Location

- (1) The California polyester resin/fiberglass industry consists of a relatively large number of small firms which, in combination, account for only a small fraction of the state's unsaturated polyester resin consumption; and a few very large firms, which use the great majority of the total resin.
- (2) Resin use per firm ranges from 99.8 kg/yr to 8.8 million kg/yr (220 lb/yr to 19.3 million lb/yr). The median firm size is 27,500 kg/yr (60,200 lb/yr).
- (3) The largest 10 percent of the users in California consume 72 percent of the unsaturated polyester resin.
- (4) At least one polyester resin/fiberglass fabricator was identified in 32 of California's 58 counties.

- (7) Continuous lamination and pultrusion processes use the most resin per firm.

1.1.4 Cross-Linking Agents and Catalysts

- (1) All but three plants reported that they used styrenated resin or did not know the cross-linking agent.
- (2) The three exceptions all use methyl methacrylate. Since two of these are among the largest in the state, methyl methacrylate accounts for about 12 percent of the monomer use.
- (3) All but eight percent of the firms in the state use methyl ethyl ketone peroxide (MEKP) as a catalyst. The second most commonly-used catalyst is benzoyl peroxide (BP).
- (4) There did not appear to be any clear pattern of catalyst use among processes or products, except that firms using BP tend to be quite large.

1.2 DEVELOPMENT OF EMISSION FACTORS

1.2.1 Definition

Given the varying emission potential of different polyester resin/fiberglass manufacturing processes and the wide range of monomer content, uniform emission factors based upon resin mass may lead to inaccurate emissions estimates. We chose to develop emission factors for each process and to define them as (mass VOC emitted)/(mass VOC input).

1.2.2 Literature Review

- (1) Data from Dade County (Florida) Department of Environmental Resources Management field tests, Bay Area Air Quality Management District source tests, Ashland Chemical Company laboratory tests, Shasta County Air Pollution Control District laboratory tests, and extensive laboratory tests by the Kingston Polytechnic Institute (England) were reviewed.
- (2) Emission factors based upon the above definition were calculated from the data obtained through the literature review.
- (3) Calculated emission factors varied widely with process and with experimental conditions.

1.2.3 SAI Source Tests

SAI conducted source tests at three representative polyester resin/fiberglass fabrication plants. In each case, grab samples were collected on charcoal adsorbent and later analyzed by gas chromatography. In two cases (Plants B and C), instantaneous concentrations measured with a portable flame ionization detector and recorded on a strip chart were integrated and then correlated with concentrations determined from charcoal trap samples taken concurrently. The average exposure during the test period could then be calculated by integrating the strip chart trace.

Source Tests at Facility A

Facility A is a large (3.6 million lb/yr) continuous lamination plant. An incinerator is used to control emissions from the impregnation table. Our findings were as follows:

- (1) Styrene concentrations at the plant's 7 emission points ranged from 2 to 1100 ppm.
- (2) Annual emissions are estimated to be 7 to 9 tons.
- (3) The monomer-based emission factor for continuous lamination without emission controls was 0.059 to 0.13. With the afterburner in use, the emission factor for this plant was 0.0092 to 0.028.

Source Tests at Facility B

Facility B is a medium size (125,000 lb/yr of resin and gel coat) tank coating plant having no emission controls. All workplace air exits the plant through a single stack equipped with a fan. Resin and gel coat are applied to the tanks with spray guns and chopper guns. Our findings were as follows:

- (1) Styrene concentrations in the 1.5-m³/s (3200 cfm) plant exhaust varied from 82 ppm (during a time of no spraying) to 405 ppm.
- (2) Given the large moment-to-moment fluctuation in the exhaust styrene concentration, it was necessary to use our integrated sampling method over a typical spraying cycle.
- (3) Styrene mass emission rates during the spraying cycle ranged from 11 to 14 lb/hr.
- (4) Emission factors for the spraying operation ranged from 0.092 to 0.13.

Source Tests at Facility C

Facility C is a large (420,000 lb/yr of resin and gel coat) synthetic marble plant. Gel coat is sprayed in a booth equipped with an exhaust fan. No exhaust gas treatment equipment is installed. Our tests covered production runs using normal resin and resin containing a vapor suppressant additive. Our findings were as follows:

- (1) Styrene concentrations in the exhaust air ranged from 10 to 22 ppm. It was not possible to determine the relative contributions of the casting resin and the gel coat.
- (2) As with Facility B, it was necessary to use our integrated sampling method to determine an average emission rate.
- (3) Styrene mass emission rates were 2.2 to 2.6 lb/hr when the normal resin was used and 1.2 to 2.6 lb/hr when the vapor-suppressed resin was used.
- (4) The monomer-based emission factors for the normal and vapor-suppressed cases were 0.026 to 0.31 and 0.014 to 0.030, respectively.
- (5) The fact that the lower bound of the emission factor estimate is lower for the vapor-suppressed resin than for the conventional casting resin is probably due more to the uncertainty in the correlation between charcoal trap styrene concentrations and flame ionization detector readings than to a real difference in emissions.

1.2.4 SAI Laboratory Tests

- (1) Under our test conditions, styrene emissions from the vapor-suppressed resins we tested were lower than those for most of the non-suppressed resins.
- (2) Long-term cumulative weight loss from the test samples was inversely related to the percentage of catalyst used.

1.2.5 Recommended Emission Factors

The following recommendations are for cases in which vapor suppressant is not used. After reviewing the literature and discussing the effectiveness of vapor suppressants with other researchers, we concluded that emission factors for vapor-suppressed resins would be 50 to 70 percent of the values reported here.

- (1) For hand layup, the monomer-based emission factors are 0.16 to 0.35 for laminating resin and 0.47 for gel coat.
- (2) For spray layup, the emission factors are 0.09 to 0.13 for laminating resin and 0.16 to 0.35 for gel coat.
- (3) For marble casting and other closed molding operations, the emission factors are 0.01 to 0.03 for casting resin and 0.26 to 0.35 for gel coat.
- (4) For continuous lamination, pultrusion and filament winding, the emission factors are 0.06 to 0.13 for resin and 0.26 to 0.35 for gel coat. (Note that gel coat is rarely used in the first two processes.)
- (5) Whenever possible, emission factor ranges should be used to estimate ranges of emissions, so that uncertainty may be explicit. Single values (such as the midpoints of the stated ranges) should be used with caution.

1.3 ESTIMATED ORGANIC VAPOR EMISSIONS IN CALIFORNIA

1.3.1 Emissions by Geographic Unit

- (1) Organic vapor emissions from polyester resin/fiberglass fabrication were estimated to be 1.41 to 2.55 million kg/yr (1549 to 2805 tons/yr) for the whole state.
- (2) Los Angeles, Orange and San Diego Counties are responsible for 81 percent of the statewide emissions. Emissions for these counties are 262 to 512, 856 to 1478 and 143 to 272 tons/yr, respectively.
- (3) The South Coast Air Basin accounts for 1152 to 2042 tons/yr, or about 73 percent of the statewide total.

1.3.2 Distribution of Emissions by Firm Size

- (1) About three quarters of the firms in California account for only about 12 percent of the emissions.
- (2) On the other hand, only 4 percent of the firms account for 50 percent of the total.

1.3.3 Distribution of Emissions by Product and Production Process

- (1) Operations in which resin spraying is used alone or in combination with other processes are responsible for about 47 percent of the state's total emissions.
- (2) Hand layup and continuous lamination processes are also significant emission sources, the former because they have high emission factors, and the latter because they are used in some of the state's largest plants.

1.3.4 Perspective

- (1) Estimated emissions from polyester resin/fiberglass fabrication in California constitute 0.054 to 0.098 percent of the total organic gas (TOG) emissions, and 0.075 to 0.13 percent of stationary source TOG emissions, as reported in the 1979 Statewide Emission Inventory.
- (2) Polyester resin/fiberglass emissions comprise about 0.66 to 1.2 percent of stationary source TOG emissions within the South Coast Air Basin, and constitute 2.8 to 4.9 percent of the total for Orange County.
- (3) It is difficult, if not impossible, to compare our estimates with those reported in various emission inventories by manufacturing category, since polyester resin/fiberglass operations have heretofore been placed under several unrelated and often incorrect categories.

1.4 REVIEW OF EMISSION CONTROL TECHNOLOGY

1.4.1 California Survey Results

- (1) Except for two continuous lamination plants which are equipped with incinerators, organic vapor removal equipment is not used in this industry.
- (2) Vapor-suppressed resins are used by 54 companies, representing 25 percent of the statewide polyester resin and gel coat use.
- (3) There was no statistically significant relationship between production type and vapor suppressant use.
- (4) Only 38 firms, representing less than 5 percent of statewide resin use, use natural ventilation to control indoor exposures; the remainder have some form of forced air ventilation.

1.4.2 Changes in Existing Processes

- (1) Emissions can be reduced significantly by using resins with lower monomer content, changing from open to closed molding, reducing rollout time, and improving housekeeping practices.
- (2) The costs of such process and material changes could range from negligible to major, depending upon the amount of retooling required.
- (3) Care must be taken that product quality is not degraded by the changes.

1.4.3 Vapor Suppressants

- (1) The trend in vapor suppressants is away from aliphatic waxes and towards combinations of new resin formulations and polymeric additives.
- (2) Laboratory and field tests of the effectiveness of vapor suppressants give widely varying results; we have assumed in our emission calculations that these additives reduce styrene emissions by 30 to 50 percent.
- (4) An informal survey of California users of vapor-suppressed resin identified potential delamination as the most feared drawback of using these additives. Some manufacturers encountered serious problems, while others did not.
- (5) Studies in Sweden have shown the effectiveness of installing a peelable material in the resin as it cures; peeling away the material permits secondary bonding without the need for sanding.

1.4.4 Incineration

- (1) At facility A, a direct flame afterburner removed 98.4 to 98.8 percent of the styrene and methyl methacrylate in that portion of the plant exhaust which was treated.
- (2) Unless recuperated heat can be used in a plant, incineration results in a large waste of energy. Polyester resin/fiberglass fabrication processes which could use recovered heat include heat curing in general, continuous lamination, pressure bag

molding, and some forms of filament winding.

- (3) The use of catalytic incinerators could lower energy requirements. Poisoning of the catalyst by metallic salts in resin promoters may present a problem.
- (4) Costs for using incineration in hypothetical small and large facilities used in our cost analyses range from \$10.3 to \$15.9 per lb styrene removed if no credit for heat recovery is assumed. With 50 percent heat recovery (which is unlikely for all but a few large plants) the cost could be as low as \$7.8/lb.
- (5) There is no economy of scale in using this control technique. Rising natural gas prices could increase costs significantly, since variable operating costs are a high percentage of the total.

1.4.5 Carbon Adsorption

- (1) Carbon adsorption has been used, with apparent success, to control styrene emissions from a fiberglass pipe collar plant in Washington State.
- (2) Potential problems with activated carbon adsorption include overheating of the adsorbent, polymerization of styrene, and clogging by particulate matter. Also, unless styrene can be efficiently recovered from the steam condensate after desorption, a liquid waste problem must be dealt with.
- (3) Of the three techniques subjected to our cost analysis, carbon adsorption had the lowest cost, \$4.3 to \$4.6/lb styrene removed, assuming no credit for recovered styrene. At today's styrene prices, credits for recovered monomer would not offset the treatment cost significantly.

1.4.6 Absorption

- (1) To our knowledge, absorption has never been used to control emissions from polyester resin/fiberglass fabrication.
- (2) Absorption equipment manufacturers expressed doubts about the applicability of this technique, since styrene is relatively insoluble in water and use of organic absorbent solutions would create air pollution and liquid waste disposal problems of their own.

- (3) An Oklahoma company built a pilot plant to assess the feasibility of using dibutyl phthalate as the absorbent medium. High capital costs have delayed construction of a full-scale scrubber.

1.4.7 Condensation

- (1) The only practical way to condense styrene vapors from plant exhaust would be to use surface condensers with a refrigerated coolant.
- (2) Condensation is generally best applicable to waste gas streams having higher organic vapor concentrations than are normally encountered in the polyester resin/fiberglass industry.
- (3) According to our analysis, the costs of removing styrene by condensation would be about \$7.3 to \$15/lb styrene removed, provided that no credit was obtained for recuperated styrene. Credits for styrene would reduce total costs to \$6.7 to \$14.4/lb.

1.5 MATERIAL TESTING

- (1) Standard ASTM procedures were used to perform interlaminar shear strength and bending tests on five resin and glass laminates.
- (2) There was no significant difference in mean interlaminar shear strength between the groups of laminates made with vapor-suppressed and non-vapor-suppressed resins. However, in the one "head-to-head" comparison of suppressed and non-suppressed resins, the laminate made with the suppressed resin had a 9-percent higher shear strength.
- (3) The use of a vapor-suppressed resin for secondary bonding after a 24-hour wait resulted in a slightly greater interlaminar shear strength than when the laminate was made in one stage with the same vapor-suppressed resin.
- (4) Correlation between bending modulus and interlaminar shear strength was rather low.

- (5) The use of vapor suppressant evidently did not affect the flexibility of the laminates.
- (6) An appreciable fraction (9 of 30) of the test specimens failed in tension, rather than in shear. Mixed mode failures are common in composites of this type.

1.6 CONTROL STRATEGY FORMULATION

- (1) Only two local air pollution control districts have regulations specifically applicable to polyester resin/fiberglass fabrication. Because styrene is sometimes used as a diluent as well as a cross-linking agent, many districts place this type of fabrication under their solvent regulations.
- (2) Any control strategy, whether it be at the state or the local air pollution control district level, should take into account the heavy concentration of emissions among a relatively small number of large firms.
- (3) A strategy based upon setting maximum levels of emissions would affect only the largest firms in the state. Compliance would be expensive for these firms, since extensive retrofitting would be necessary in some cases.
- (4) An approach based upon requiring a certain percentage of removal of organic vapors from all firms (or all firms whose emissions would otherwise exceed a minimum level) would place a heavy burden on smaller firms, while net emission reductions from the industry would be lower than if absolute emission standards were used.
- (5) Industry-wide technology-based standards are inadvisable, since the requirements for, and applicability of, different types of equipment vary with fabrication process.

RECOMMENDATIONS

On the basis of our findings in this study, we make the following recommendations.

- (1) The information obtained through our survey of the California polyester resin/fiberglass industry (and provided to the Air Resources Board as a separate document) should be incorporated into local emission inventories and the statewide Emission Data System (EDS). Furthermore, the ARB should establish category of emission source (CES) numbers for the several polyester resin/fiberglass fabrication processes, so that speciated emissions from these sources can be identified unambiguously in the EDS.
- (2) Emission factors for the processes used in this industry should be (a) process-specific and (b) based upon the amount of cross-linking agent (e.g. styrene or methyl methacrylate) used in the process, rather than upon the total amount of polyester resin and/or gel coat. This approach will give a more accurate estimate of the uncontrolled emission potential.
- (3) Any emission regulations covering this industry should recognize that styrene, methyl methacrylate and other cross-linking agents are not used primarily as solvents.
- (4) Since only 4 percent of the polyester resin/fiberglass fabricators in California account for half the emissions from this type of source, any regulatory strategy should focus upon these plants.
- (5) Changes in production process, use of low monomer resin, implementation of better housekeeping, and other relatively inexpensive but often highly effective measures should be encouraged wherever feasible.
- (6) Resins containing vapor suppressant additives may be used as part of an overall emission control strategy, with the caveat that the potential user conduct thorough tests of material properties specific to the product to be manufactured.
- (7) Carbon adsorption should be evaluated further as a means of controlling styrene emissions, especially from large sources.

3.0

INTRODUCTION AND BACKGROUND

3.1 INTRODUCTION

3.1.1 Purpose and Objectives of the Study

It has long been recognized that production of reinforced plastic materials through the combination of polyester resin/styrene mixtures and glass fibers results in the release of significant quantities of styrene vapors into the workplace air. In order to reduce workplace concentrations, fabricators commonly vent the styrene and other organic emissions to the outside air. Because styrene and the most common catalyst used in these processes, methyl ethyl ketone peroxide, are both photochemically reactive substances, there is concern that their release to the atmosphere may contribute to photochemical smog formation. There are at present no federal or state emissions standards for styrene for the reinforced plastics source category. Local air pollution control districts' control strategies vary considerably.

The objectives of the study were (1) to locate and characterize as many sources of polyester resin/fiberglass process emissions in California as possible; (2) to establish an emission inventory based upon realistic emission factors for the pollutants of interest; and (3) to review the technology for controlling organic vapor emissions from this industry.

3.1.2 Outline of the Research

Research under this contract was conducted between June 1980 and October 1981. The major elements of the study were as follows.

Emission Inventory Survey

Before this project, no comprehensive, detailed inventory of polyester resin/fiberglass fabricators existed. We therefore attempted to identify and obtain information from several hundred firms which were initially believed to be polyester resin users. The result of our survey, which was conducted through written questionnaires and telephone interviews, is a data base covering more than 300 California polyester resin/fiberglass fabricators. This portion of the research is described in Chapter 4.

Derivation of Emission Factors

Organic vapor emissions from polyester resin/fiberglass processes have traditionally been estimated by multiplying polyester resin use rates by "rule-of-thumb" emission factors. Because the potential for emissions varies with resin composition and production process type, using one or two emission factors for all cases can lead to serious errors. In order to develop more accurate and useful emission factors, we:

- Used data from previous field and laboratory work;
- Measured exhaust emissions from California plants which used three different production processes; and
- Performed laboratory tests of organic vapor emissions from resins containing vapor suppressant additives.

Our discussion of the derivation of emission factors is presented in Chapter 5. In Chapter 6, these factors are used in conjunction with industry survey data to estimate organic vapor emissions in California.

Review of Control Technology

Organic vapor emissions from polyester resin/fiberglass fabrication processes may be reduced by process changes, use of vapor-suppressed resin, or exhaust gas cleanup technology. With only a handful of exceptions, the first two approaches are the only ones currently taken by California plants. In this portion of the study we reviewed the applicability and costs of process changes, vapor suppressants, incineration, adsorption, absorption and condensation techniques. Because concern over the effect of vapor suppressant use on product quality had been expressed, we also conducted material tests on laminates made from various resin formulations. Our review of control technology is presented in Chapter 7. Chapter 8 contains our estimates of the costs of various control strategies, and Chapter 9 describes our materials testing. Control recommendations are presented in Chapter 10.

3.2 POLYESTER RESIN COMPOSITION, PROPERTIES AND USE TRENDS

Given the complex nature of the reinforced plastics industry, it is important to define carefully the scope of this study. As used here, the term "polyester resin/fiberglass" will mean a material composed of a cured, cross-linked polyester resin, a reinforcing agent and/or inorganic fillers. Figure 3.2-1 shows how various chemicals are combined to form the types of reinforced

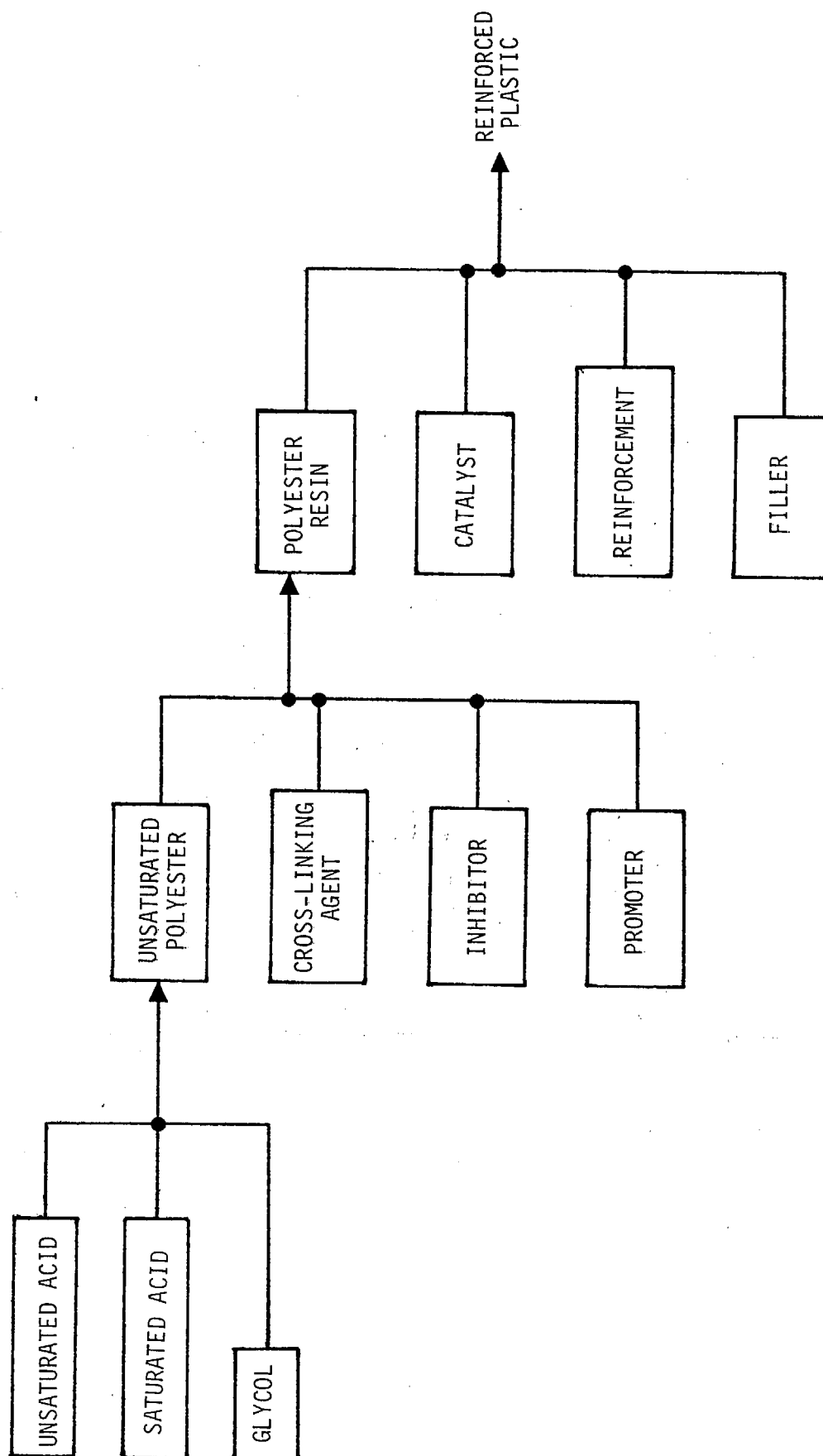


Figure 3.2-1 Composition of Unsaturated Polyester, Polyester Resin and Reinforced Plastics of Interests

plastics of interest. Although we are concerned only with organic vapor emissions from the third column of the flow chart, polyester resin/fiberglass fabrication, an understanding of unsaturated polyester and polyester resin formulation is essential.

3.2.1 Polyester Resin Composition and Chemistry

We further restrict the scope of this study to what are known in the plastics industry as thermosetting, unsaturated polyester resins. Polyester resins are complex polymers consisting of a liquid unsaturated polyester and a vinyl-type monomer. That they are thermosetting means that they cannot be softened by heat after they are cured (Shreve and Brink, 1977); indeed application of high temperatures to cured thermosetting resins tends to degrade the material. The polyester resins polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are formed without cross-linking monomers and are therefore excluded from consideration, although they are discussed briefly at the end of this section.

Unsaturated Polyester

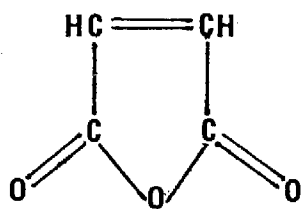
Unsaturated polyester is formed from the condensation of an unsaturated dibasic acid or anhydride, a saturated dibasic acid or anhydride, and a polyfunctional alcohol. Table 3.2-1 lists the most common chemicals used for each component of the polyester "backbone." Structures of some of these compounds are shown in Figures 3.2-2 through 3.2-4.

The purpose of the unsaturated acids is to provide double bond sites for reaction with cross-linking agents. Maleic anhydride is a common choice for the unsaturated acid because it will not homopolymerize, even at high temperatures, but will rapidly react with vinyl monomers, such as styrene. Especially important is the fact that maleic anhydride reacts more quickly with styrene than styrene does with itself (Kent, 1974).

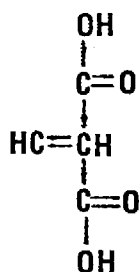
Saturated acids are added to impart various desired properties to the final product. Phthalic anhydride increases flexibility and, because it is relatively inexpensive, lowers the overall costs of the resin. Isophthalic anhydride imparts good tensile strength and resistance to weathering and corrosion; it is frequently used in the manufacture of chemical storage tanks, ducts, and cooling tower louvers. Isophthalic resins are also used to make the molds on or in which other polyester resin/fiberglass products are fabri-

Table 3.2-1
COMPONENTS OF UNSATURATED POLYESTER

Unsaturated Acids	Saturated Acids	Alcohols
Maleic anhydride	Phthalic anhydride	Propylene glycol
Fumaric acid	Isophthalic anhydride	Ethylene glycol
	Adipic acid	Diethylene glycol
		Dipropylene glycol
		Pentaerythritol

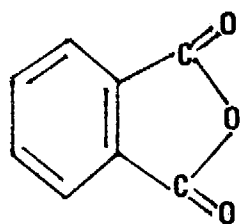


Maleic anhydride

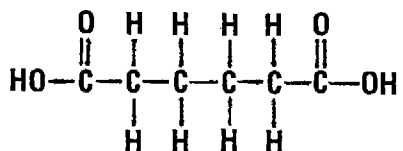


Fumaric acid

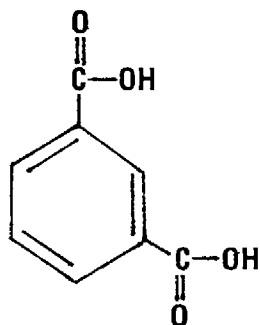
Figure 3.2-2 Structures of Some Common Unsaturated Acids



Phthalic anhydride



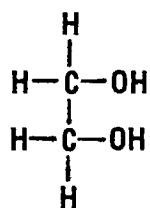
Adipic acid



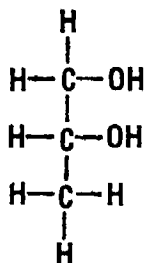
Isophthalic acid

Figure 3.2-3 Structures of Some Common Saturated Acids

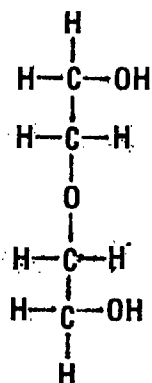
POLYFUNCTIONAL ALCOHOLS



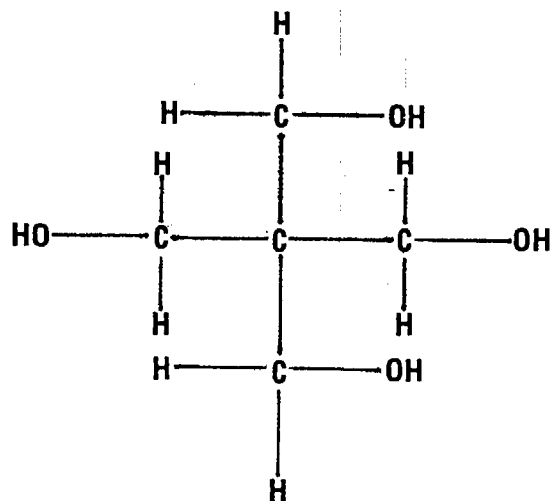
Ethylene Glycol



Propylene glycol



Diethylene glycol



Pentaerythritol

Figure 3.2-4 Structures of Some Common Polyfunctional Alcohols

cated, and are a component of 95 percent of the gel coats used in the marine industry (Edwards, 1979). Adipic acid, because of its long flexible aliphatic carbon chain, is used when a high degree of flexibility is desired. By lowering the concentration of double bonds, the saturated acids also alter the reactivity of the polyester (Czarnomski, 1979). The molar ratio of the saturated to unsaturated acid varies but is commonly between 1:1 and 1:1.5 (Kent, 1974).

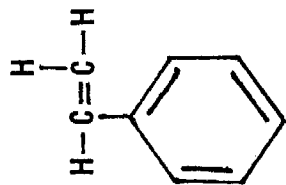
The third constituent of the unsaturated polyester backbone is the polyfunctional alcohol. Ethylene glycol is commonly used. It is frequently supplemented with propylene glycol, diethylene glycol, or dipropylene glycol to decrease the tendency for the liquid resin to crystallize and to increase the flexibility of the cured resin (Kent, 1974). According to Edwards (1979), gel coats composed of neopentyl glycol in combination with isophthalic acids have the best weatherability.

Cross-linking Agents

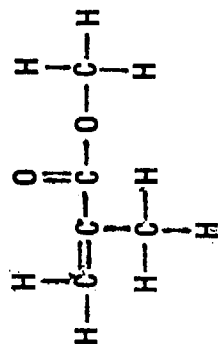
Unsaturated polyesters generally do not undergo homogeneous polymerization, even at high temperatures. In order to form a resin, therefore, it is necessary to add a cross-linking agent. Figure 3.2-5 shows the structures of several monomers used for this purpose, while Table 3.2-2 summarizes their properties. The most common cross-linking agent by far is styrene. According to our survey, the next-most frequently used monomer in California is methyl methacrylate. Vinyl toluene ranks a distant third. These compounds are discussed further in Section 3.2.2.

Figure 3.2-6 depicts a typical cross-linking reaction. Cross-linking requires the formation of three types of radicals: those of the unsaturated acid, the cross-linking monomer, and a catalyst. If temperature is applied to the resin mixture, then the catalyst decomposes thermally and initiates the reaction. At room temperature, however, it is necessary to add a "promoter" or "initiator." These components are discussed below.

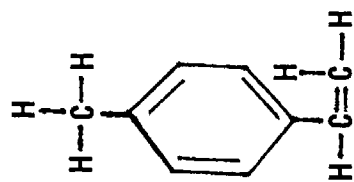
In a typical resin, about 95 percent of the unsaturation sites are reacted with the cross-linking agent (Boenig, 1964). It should be noted that both monomer-unsaturated acid and monomer-monomer reactions occur. In the case of styrene, an average of two monomers link up to form a bridge between two segments of polyester backbone.



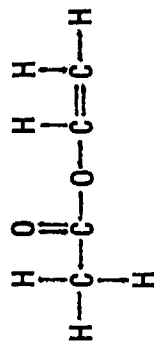
Styrene



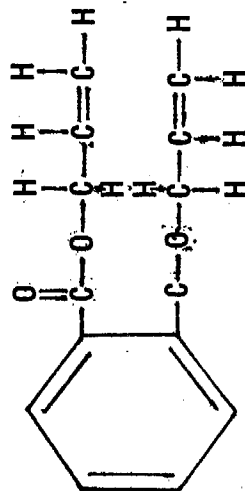
Methyl Methacrylate



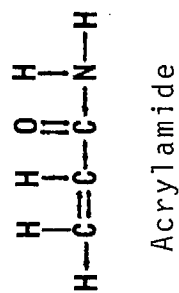
Vinyl Toluene



Vinyl Acetate



Diallyl Phthalate



Acrylamide

Figure 3.2-5 Structures of Some Common Cross-Linking Agents in Polyester Resin

Table 3.2-2
PROPERTIES OF CROSS-LINKING AGENTS IN POLYESTER RESIN

Compound	Molecular Weight	Boiling Point, °C	Characteristics
Styrene	104.14	145.2	Good reactivity, low cost, wide availability
Methyl methacrylate	100.11	145.2	Reduced resin viscosity, improved optical qualities, improved weather resistance
Vinyl toluene	118.18	172	Short cure time, higher resin viscosity, higher cost
Vinyl acetate	86.1	72	Highly volatile. Poor weather and water resistance
Diallyl phthalate	246.25		Requires high-temperature cure; higher resin viscosity, high cost; lower volatility during cure
Acrylamide	71.08	(solid)	Water soluble, requires pressure, not a solvent
2-ethyl hexylacrylate	184.3	215	Mild irritant, flexibilizes resin, high cost

Source: Brighton et al., 1979; Verschueren, 1977

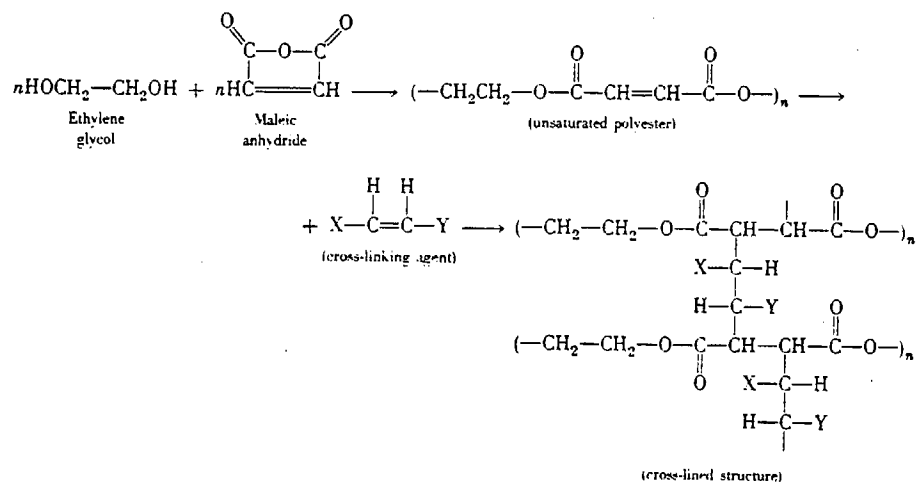


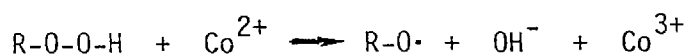
Figure 3.2-6. Typical Cross-Linking Reaction for Polyester Resin Formation.

Catalysts, Inhibitors and Promoters

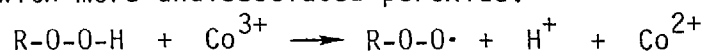
Although methyl ethyl ketone peroxide (MEKP) and other such reagents are commonly called "catalysts" in the industry, they are more correctly termed polymerization initiators, since the free radicals generated become chemically bonded to the crosslinked resin (Lucidol, 1980). Our industrial survey (see Chapter 4) found that about 92 percent of the firms in California use MEKP, and that these firms account for about three quarters of the state's polyester resin use. The only other catalyst used to any appreciable extent is benzoyl peroxide (BP), which is commonly associated with high-temperature cures. Catalysts used in a few places include cumene hydroperoxide; peroxydicarbonate; and 2,4-pentanedione peroxide. Catalyst concentrations generally range from 1.0 to 2.0 percent by original weight of resin, depending upon desired gel time; the higher the catalyst concentration, the faster the cross-linking reaction proceeds.

Although the reaction rate is slow, polyester resins will self-cure without a catalyst if given enough time. The exothermic nature of the reaction could lead to explosion and/or fire if the resins are not stored properly. To avoid these problems, resin manufacturers add inhibitors such as para-tertiary-butyl-catechol and hydroquinone. Other inhibitors include phenolic resins, aromatic amines, pyrogallol, chloranil, and picric acid (Anon., 1970). It should be noted that oxygen is a powerful inhibitor.

The function of promoters is to activate decomposition of the peroxide catalyst. Common catalyst/promoter combinations include MEKP/cobalt naphthenate, MEKP/cobalt octoate, and BP/diethyl aniline, (Czarnomski, 1979). The reaction between the catalyst and the cobalt initiator is:



The cobaltic ion generated by this reaction is reduced to its original form by reaction with more undissociated peroxide:



Promoters reduce the temperature at which the catalyst normally thermally decomposes and thus initiate the cross-linking reaction at lower temperatures (Gallagher and Kamath, 1978). Since mixing cobalt salts and catalyst directly is dangerous, most resin manufacturers now add promoters to the resin before sale; such resins are called "promoted."

Other Additives

A wide variety of organic and inorganic compounds are added by resin manufacturers and users to obtain desired product properties. The following discussion is, except where otherwise noted, based upon a review by Czarnomski (1979). Thixotropic agents such as pyrogenic silica are added to permit the fabricator to apply resin to vertical mold surfaces without the problem of dripping. Resin extenders, which are usually added by the polyester resin/fiberglass fabricator, reduce cost, modify physical properties, reduce shrinkage during cure and provide or increase flame retardance. The most common extenders, which are used heavily in the artificial marble industry, include alumina trihydrate (ATH), calcium carbonate, and various clays and talcs. Antimony oxide is also used. Aluminum alkoxid compounds may be used to eliminate the clouding that sometimes results from impurities in phthalic anhydride (Anon., 1978a). One chemical manufacturer claims that addition of dicyclopentadiene (DPCD) to polyester resin lowers the resin density (allowing lower resin use) while conserving mechanical properties (Nelson, 1978).

Polyester-Based Materials Not Considered

As polyester is a component of several important reinforced plastics not considered in this study, it is worthwhile to described them briefly and explain why they were excluded. Foamed polyester, which is not yet used to an important extent in California but which could be a styrene-saving substitute for many conventional liquid unsaturated polyester formulations, is discussed in Section 3.3.8.

Sheet Molding Compound (SMC). Sheet molding compound is a one-component molding system consisting of polyester resin, extenders, catalysts, release agents, pigments and glass fibers (Czarnomski, 1979). It is formed by impregnating the glass fiber with a "paste" composed of the other ingredients and compressing the mixture between polyethylene sheets (Lichtenberg, 1979). A typical use of SMC in fabrication is to compress it in matched-die molds. Up to now, the principal products made with SMC have been automobile parts, including front end panels, head lamp housings, spoilers, window frames, air deflectors and wheel covers. The auto industry is considering SMC formulations having 60 percent glass fibers (as opposed to the more typical 20 to 30 percent) for structural parts such as transmission and radiator supports (Czarnomski, 1979). Many new uses are reported in the trade journals; these

include laundry tubs, machine housings, bathtubs, house sidings and shutters, welding helmets, and a variety of other products. SMC was excluded from the study because both the means of formulation and application appear to have a low potential for organic vapor emissions.

Bulk Molding Compound (BMC). Bulk molding compound is prepared by blending short (0.3 to 1.3-cm) glass fibers with polyester resin, fillers, and other additives into a putty- or dough-like consistency. BMC can be blended by the fabricator or bought in bulk to be used in compression and injection molding, or used as solid pellets or extruded preforms in compression or transfer molding (Lichtenberg, 1979). Typical products made with BMC include automobile distributor caps, circuit breaker housings, and other electrical parts. BMC was excluded because it is a thermoplastic material and has a low potential for organic vapor emissions.

Other Thermoplastic Polyesters. A material of increasing popularity is polyethylene terephthalate (PET), a thermoplastic polyester (Kirshenbaum and Rhodes, 1979). Most of the growth in use of PET in recent years has been in the beverage container industry, although it has been used for quite some time in food packaging film, clothing, carpeting and tire cord. No cross-linking agent is used in formulation or fabrication.

Polybutylene terephthalate (PBT) is another thermoplastic polyester. It is formed from the polycondensation of 1,4-butanediol and dimethyl terephthalate (Avery, 1979). Since it is a solid at room temperature and is used in injection molding, the potential for organic vapor emissions is quite low.

Copolyesters. Copolyesters are synthesized from more than one glycol and/or more than one dibasic acid (Rich, 1979). An example is a polyester copolymer based on terephthalic acid (PCTA), which is composed of cyclohexanedimethanol, terephthalic acid, and another acid, and is used for making packaging film. Copolyesters are solids at room temperature and have either a crystalline or an amorphous structure, depending upon their ingredients. They do not contain low-molecular-weight cross-linking agents and therefore have a low organic vapor emission potential.

3.2.2 Compounds of Potential Air Pollution Concern

The most important component of unsaturated polyester resin systems is styrene, since it is volatile, heavily used, and photoreactive. The

following discussion, except where otherwise noted, is based upon a review of styrene and other alkyl benzenes by Santodonato et al. (1980). The chief properties of concern are styrene's odor threshold and its photoreactivity. One of the chief problems with styrene emissions, especially from facilities in or near residential areas, is that the compound can be detected at very low ambient concentrations. Estimates of odor threshold vary from 0.036 mg/m^3 (Verschuere, 1977) to 0.34 mg/m^3 (Smith and Hochstetler, 1969). (At 25°C , these concentrations correspond to 8.4 and 80 ppb.) The higher of these two values has been reported by May (1966).

On the few occasions when they have been measured in ambient urban air, styrene concentrations have generally been below 10 ppb. Table 3.2-3 lists the concentrations measured by Neligan et al. (1965) in Southern California air. Concentrations in Los Angeles were below the 0.5-ppb limit of detection of the flame ionization gas chromatography method used. By reacting styrene with bromine and analyzing the resulting styrene dibromide with an electron capture detection system, Hoshika (1977) was able to detect styrene concentrations as low as 0.1 ppb. Concentrations of 0.2 ppb were measured in urban air in Japan by this technique.

Styrene does not absorb ultraviolet radiation with wavelengths greater than about 300 nm. It is therefore not likely to be photochemically decomposed by direct absorption of sunlight near the earth's surface. However, according to Santodonato et al., styrenes and ethylbenzenes "are among the most active generators of photochemical smog." The most important reaction is electrophilic addition (by atomic oxygen, ozone and other oxidants) to the olefinic double bonds. Santodonato et al. predict, in the absence of actual data, that the final reaction products would be peroxides, formaldehyde and benzaldehyde. The rate of reaction of styrene with hydroxyl radical has been estimated to be $7390 \text{ ppm}^{-1} \text{ min}^{-1}$ (Atkinson et al., 1981). This rate is considerably lower than those for alkanes (generally 10000 to 20000 $\text{ppm}^{-1} \text{ min}^{-1}$), aldehydes (14000 to 46000 $\text{ppm}^{-1} \text{ min}^{-1}$), and other alkylbenzenes (20000 to 60000 $\text{ppm}^{-1} \text{ min}^{-1}$).

No data on methyl methacrylate or other cross-linking agents were available. From their structures, however, these compounds would be expected to be photoreactive also. Methyl methacrylate's odor threshold (210 ppb) is higher than that for styrene (May, 1966).

Table 3.2-3
STYRENE CONCENTRATIONS IN SOUTHERN CALIFORNIA
AMBIENT AIR SAMPLES

Location	Time	Concentration (ppb)
Azusa	0900	4
	1000	5
Burbank	0600	2
	0900	3
Inglewood	0700	8
	0730	15
Long Beach	0700	2
	0730	1
Los Angeles	0600	a
	0700	a

Source: Neligan et al., 1965 (cited in Santodonato et al., 1980).

^a Below detection limit of 0.5 ppb.

3.2.3 Trends in Use of Polyester Resin

The industry survey conducted under this project and described in Chapter 4 determined with a fair degree of accuracy how much unsaturated polyester resin was used in California in 1980-1981. The polyester resin/fiberglass industry was clearly in a slump during that period. About 15 percent of the firms believed to have been polyester resin users had gone out of business or had moved from California. Many survey respondents reported that production was less than half of normal and that their plants were operating fewer hours per day or days per week. Especially hard-hit was the marine industry, a major user of polyester resin in California. Boat sales suffered from the poor state of the economy in general, high fuel costs, and a lack of mooring spaces in Southern California, while manufacturers found land and labor costs to be lower in Florida (Byron, 1980). For the country as a whole, marine use of reinforced plastics fell by 28.6 percent from 1979 to 1980, and by 36 percent from 1978 to 1980 (Anon., 1981a).

Figure 3.2-7 shows U.S. production of unsaturated polyester resin for every year between 1970 and 1981. Between 1970 and 1973, production almost doubled; there then followed a two-year slump. Production reached a peak of 1.2 billion pounds in 1978 and declined during the next two years. The decrease between 1979 and 1980 was 17.4 percent. Another trend which can be discerned from data compiled by the Society for the Plastics Industry, Inc. (Anon., 1981b) is that unsaturated polyester resin's share of the plastics market (thermosetting plus thermoplastic resins) has declined rather steadily over the past ten years. In 1980, the resin accounted for 3.07 percent of U.S. production, compared with a high of 4.31 percent in 1973.

Industry experts have expressed optimism about a modest recovery of reinforced plastics sales during 1981-1982 (Anon., 1981a). Whether this optimism proves to be realistic will depend upon the ability of the industry to overcome the dampening effect of continued high interest rates upon purchases of products which account for a high percentage of polyester resin use, including boats, cars, houses and appliances. Among the factors which may stimulate recovery in California's boatbuilding industry--despite the high interest rates--are consistent growth in sailboat and canoe sales (even as yacht sales decline), increases in the prime boat-buying population, use of expensive yachts as investments and tax shelters, and increased use of

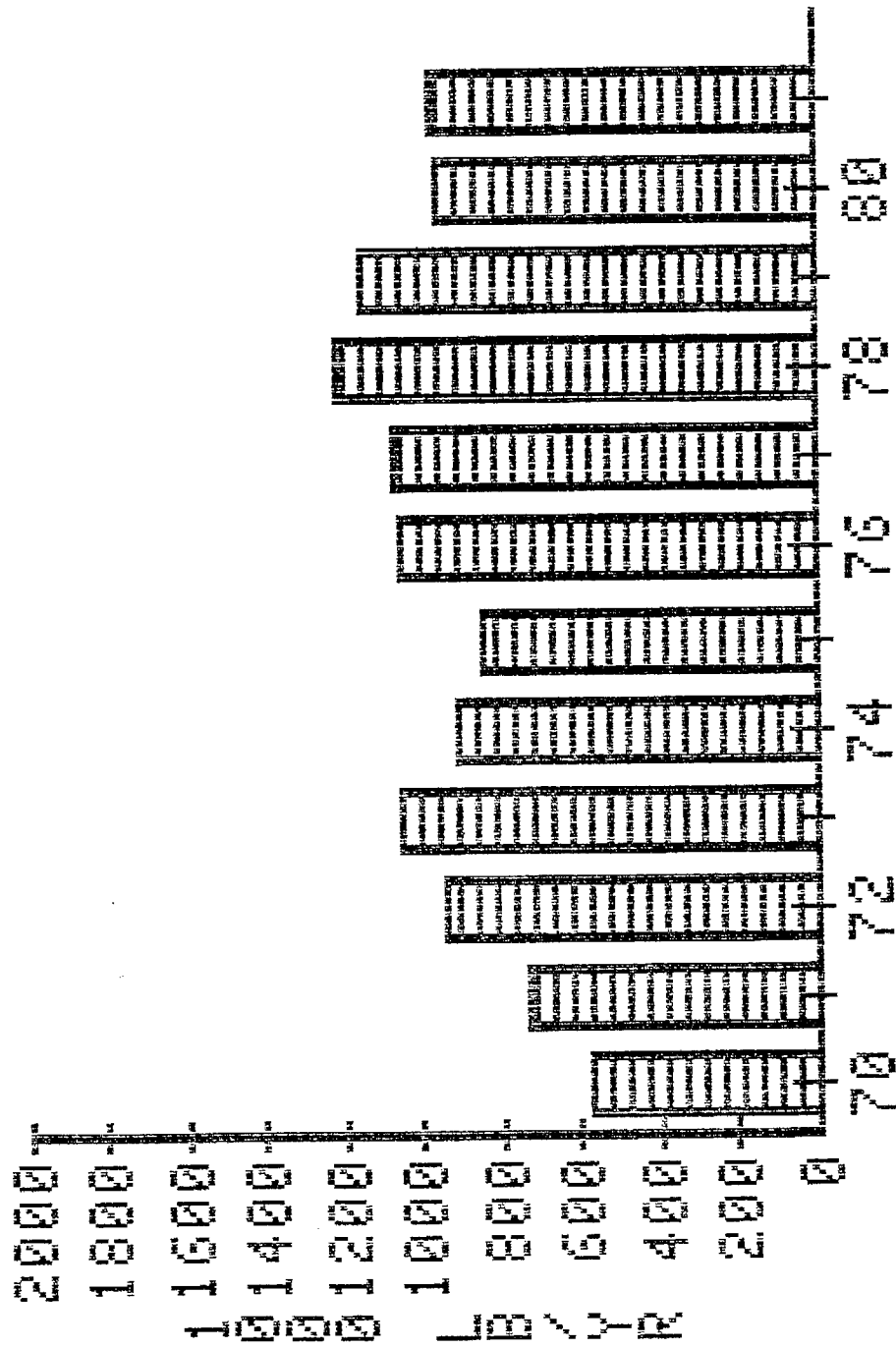


Figure 3.2-7. U.S. Production of Unsaturated Polyester Resin, 1970 - 1981 (Anon., 1981b)

fuel-efficient diesel engines in watercraft (Sing, 1981). In addition, according to one synthetic marble manufacturer we interviewed, the current slump in the home construction market is being offset by growth in sales of artificial marble for home remodeling. Increased use of thermosets in the auto industry is also expected (Anon., 1981c). Polyester resin sales declined through the first half of 1981, although the rate of decline steadily decreased; in fact, by July 1981 sales were increasing at an equivalent annual rate of about three percent (Anon., 1981d). As seen in Figure 3.2-7, this recovery continued for the rest of 1981.

Meanwhile, the trend in general-purpose polyester resin prices has been upward. The average resin price rose from 54 cents per pound in 1979 to 58 cents per pound in 1980, and is currently at 61 cents per pound (Anon., 1981d). Deregulation of the price of natural gas, from which about half of the weight of a typical polyester resin is derived, could lead to further price increases.

3.3 PRODUCTION PROCESSES

The potential for emission of organic vapors from polyester resin/fiberglass fabrication varies with the manner in which the resin is mixed, poured, manipulated and cured. In order to gain at least a qualitative understanding of the emission potential of various fabrication processes, project staff held numerous discussions with plant operators and toured seven facilities. As will be discussed in Section 4.3, our survey of polyester resin users determined that eight processes, singly or in combination, account for the vast majority of resin use in California. These are, in descending order of resin use:

- Spray layup
- Hand layup
- Continuous lamination
- Marble casting
- Pultrusion
- Filament winding
- Bag molding
- Matched metal molding

These processes, along with others which may see increasing use during the

next decade, are described in the following subsections. Along with each description, judgments of the relative potential for organic vapor emissions are presented.

3.3.1 Hand Layup

Hand layup, which is the oldest method of polyester resin/fiberglass fabrication, is used by over two-thirds of the polyester resin users in California. Figure 3.3-1 shows a typical hand layup process. The mold, which defines the shape of the outermost surface of the finished product, is itself generally made of reinforced plastic; isophthalic polyester resins are frequently used. The first step in production consists of coating the mold with a releasing agent, such as wax, to ensure that the finished product may be removed after cure. Then, in most cases, a layer of "gel coat," which consists of unsaturated polyester resin, catalyst and (optionally) colorants, is applied. Since the gel coat layer is closest to the mold, it forms the outermost surface of the finished piece. It should be noted that some products, notably surfboards, generally do not include a gel coat layer.

The next step in hand layup is the application of alternate layers of polyester resin and reinforcement material. A wide variety of reinforcements are used, but the most common are glass cloth, woven glass mat, chopped glass strand mat and preimpregnated glass cloth ("prepreg"). The ratio of resin to glass varies with the desired product properties, but is generally in the neighborhood of 60 to 40 by weight. After a reinforcement layer is placed on the mold, it is "wetted out" with resin. The new surface is then "rolled out" by hand with small rollers or squeegees to remove air pockets and other imperfections, and to assure complete contact between resin and reinforcement. The process is continued until the desired thickness is achieved. Because the cross-linking reaction is exothermic, hand layup processes do not need an external heat source to facilitate curing; room temperature cure is the most common.

The potential for organic vapor emissions from hand layup is rather high. A relatively large surface of resin and/or resin-impregnated glass is exposed to the atmosphere for most of the production cycle. Field and laboratory studies of emissions from hand layup processes are discussed in Chapter 5.

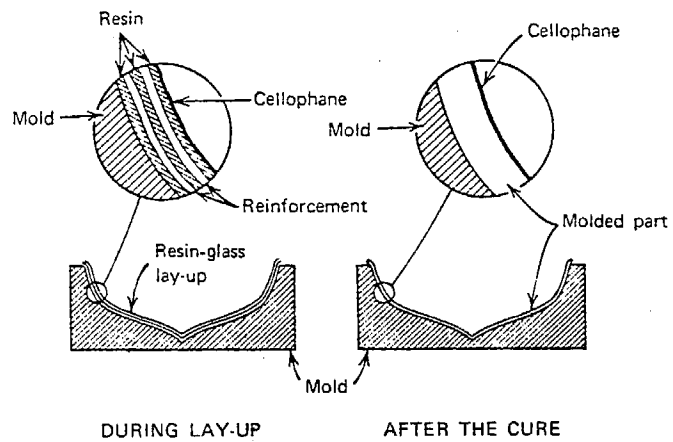


Figure 3.3-1. Typical Mold Arrangement for Hand Layup (Anon., 1970).

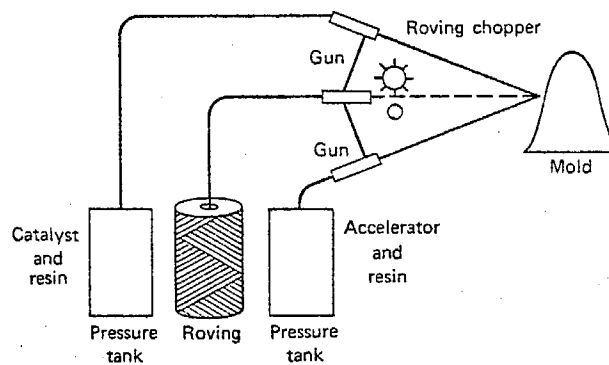


Figure 3.3-2. Schematic of Chopper Gun Molding Process (Anon., 1970).

3.3.2 Spray Layup

Our industry survey showed that about half of the polyester resin/fiberglass fabricators in California use some form of spray application of resin to a mold. In many operations, one of the first steps is to spray the mold with gel coat. Gel coat spray systems consist of separate resin and catalyst sources and an airless spray gun similar to the type used in paint spraying. The two chemical ingredients are mixed as they exit from the gun.

The other principal type of spray apparatus is the "chopper gun" system, which is depicted in Figure 3.3-2. The chopper gun contains a mechanism for cutting glass roving into pieces about one inch long; the chopped glass then mixes with the resin and catalyst streams as all materials leave the gun.

Both types of spraying are done by hand. In each case, the amount of spraying depends upon the desired thickness of the layer being applied. Since the gel coat is usually the first of several coats of resin to be applied to a mold, it is normally not allowed to cure significantly before the next step; the gel coat surface should remain "tacky," so that subsequent layers can readily adhere. Sprayed-on layers of resin and glass are often rolled out by hand, as in hand layup, to remove imperfections.

Of all the production processes reviewed here, spray layup probably has the highest potential for emission of organic vapors. Atomization of resin creates an enormous surface area for evaporation of cross-linking agent. Given the ease of operation, large amounts of resin can be applied rapidly to the mold; our survey found that plants using only spray layup use ten times more resin per plant than do those using only hand layup. Field and laboratory test data on emissions from spray layup processes are presented in Chapter 5.

3.3.3 Continuous Lamination

Continuous lamination is a substantially automated process for mass producing laminates. The following discussion is based upon descriptions by White (1979) and our own inspection of two plants which use this process. Figure 3.3-3 shows a schematic of continuous lamination. Resin and chopped glass are sandwiched between two carrier films and passed through a curing oven.

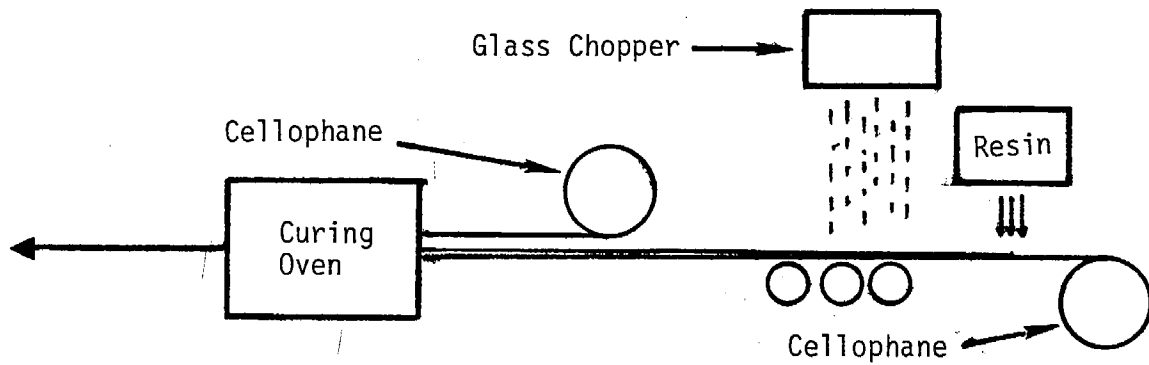


Figure 3.3-3. Schematic of the Continuous Lamination Process

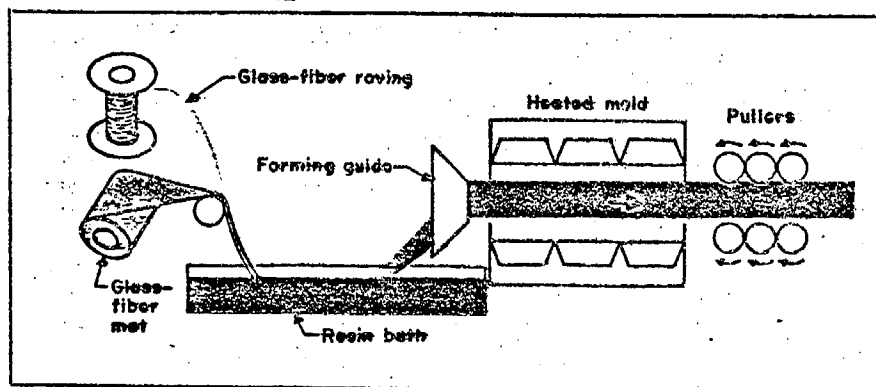


Figure 3.3-4. Schematic of the Pultrusion Process (Martin, 1989)

At the start of the process, resin is metered onto the lower carrier film, which is carried on a conveyor belt. The film, which creates the panel's outer surface, usually consists of polyester, cellophane or nylon, and can be smooth, embossed, or matte-finished. For extra weather resistance, a polyvinyl fluoride film, which permanently bonds to the polyester resin, is used. The polyester resin used in this process usually contains various additives to increase weather resistance and decrease flammability. Common fillers are calcium carbonate and aluminum trihydrate. Methyl methacrylate is sometimes used as the cross-linking agent, either alone or in combination with styrene, to increase strength and weather resistance. After the resin is spread evenly across the carrier film, chopped glass roving is made to fall over the wetted surface.

Shortly before the conveyor belt enters the curing oven, a top layer of carrier film is added. The resulting "sandwich" is pulled through a set of squeeze rollers to eliminate entrapped air and set the sheet thickness. When the laminate enters the oven, it is still very pliable. It is therefore possible to achieve various cross-sectional patterns, such as corrugation, by passing the laminate over a wooden or metal pattern, call a "shoe." Ovens are heated by electricity or gas and operate at temperatures as high as 200 °C (400 °F). When the fully-cured laminate leaves the oven, it is trimmed to its final width and cut into desired lengths by saws. The carrier films are then stripped off.

The largest use of continuous lamination is for manufacture of patio covers, awnings, fences and skylights. Depending upon the amount of filler used in the resin, the panel's light transmission can vary from none to 95 percent. Thus another large use is for greenhouse panels. Weather- and chemical-resistant panels are used as louvers in cooling towers. Uses which are increasing in popularity include covers for solar collectors, garage doors and truck/trailer liners.

In one of our field tests (see Section 5.2.3), we determined that the most important source of organic vapor emissions from this process was the impregnation table, where a thin layer of polyester resin is exposed for up to a few minutes to the atmosphere. The emission potential increases when the impregnation table is heated, as it was at one of the facilities we visited. Other emission sources are the ovens and the final sawing operations; the

latter release some uncured resin, which includes volatile organics, to the atmosphere.

3.3.4 Synthetic Marble Casting

Manufacture of synthetic marble from polyester resin is becoming increasingly popular in California. Resins used for marble production have higher viscosities and lower monomer contents than do laminating resins or gel coats. Fillers such as calcium carbonate and aluminum trihydrate are used to increase product strength and flame resistance. These fillers, along with coloring agents, are added to the resin in large rotating kettles or buckets. In some versions of casting, the mixture is poured into a female mold and stirred by hand to achieve the swirling patterns characteristic of real marble. In other cases, the resin is applied by a trowel to a male mold which has been previously covered with gel coat. A cover is then placed on the mold, and additional resin is poured between the two surfaces.

The potential for organic vapor emissions from marble manufacture is considerably lower than for other production processes, if only because the cross-linking agent content of the resin is lower (30 to 38 percent versus 40 to 48 percent for most laminating resins). Emission rates will also depend upon the extent of exposure of the curing material to the atmosphere.

3.3.5 Pultrusion

The following discussion is based upon papers by Wood (1978a), Martin (1979), and Ewald (1979). Pultrusion is a relatively new technique for making substitutes for products which are normally made by thermoplastic processes or by extruding metals such as aluminum. While equipment design varies widely, the basic process is the same: reinforcement materials are pulled continuously through first a resin bath and then a closed mold having the desired cross-sectional shape. The process is thus suitable for long products requiring a uniform cross section, although numerous short products are also manufactured.

Figure 3.3-4 is a schematic of the pultrusion process. Reinforcing material, which is usually glass roving or continuous strand glass mat, is pulled from a creel. If the product is to have high strength only along its longitudinal axis, then the reinforcement material is pulled directly through the system. For greater transverse strength, additional reinforcement may be

wrapped around the moving part. This filament wrap may be applied by a stationary creel as the part moves past, or by "overwinding wheels," which orbit around the part and apply the wrap at an angle to the direction of motion. A California firm has developed special equipment to combine winding with pultrusion (Wood, 1978a).

Resin impregnation is accomplished by passing the fibers through a resin tank bath. Polyester resin is used in at least 85 percent, by weight, of pultruded products. The composite is often preheated by application of radio frequency energy before it reaches the heated die. Occasionally, the glass fibers are heated before the resin immersion step. Dies, which are made of metal, are heated electrically with exterior surface contact strips. In some cases, the heat source is internal. The pulling device consists of a set of clamps or a caterpillar tractor. After the pultruded composite emerges from the die, it is trimmed to the desired product length with a crosscut saw; since the process is continuous, the saw must move with the product.

The main advantages of pultruded products are their high strength-to-weight ratios and good electrical insulation, thermal insulation, and corrosion resistance characteristics. Products used in the electrical industry include antennas, suspension and strain insulators, booms for electrical maintenance trucks, fuse tubes and contact rail safety covers. Pultrusion is also used to make building panel insulating strips, chemical plant grating, snowmobile track stiffeners, floor slats for livestock confinement, rail car lading bars, solar collector frames, auto steering control arms, and a variety of other products. On the negative side, pultrusion throughput rates are slower than those for thermoplastic processes. Also, the stiffness of a roving-reinforced plastic bar is low compared to that of the same shape in aluminum, even when the glass content reaches 80 percent, and pultruded products are more expensive per unit weight than those made of extruded aluminum.

The main source of organic vapor emissions in pultrusion would be the resin impregnation bath, since curing takes place in the enclosed mold. The bath configuration could have a significant effect upon the potential for emissions. Long, narrow, deep baths would present the minimum surface area to atmospheric contact. Resin use can be minimized by pumping resin into the tank in carefully controlled amounts as the reinforcement fibers pass through.

If only longitudinal reinforcement is required, then the tank could be substantially enclosed; however, it would be difficult to enclose a system which included an overwinding apparatus. In addition, as one pultruder firm pointed out to us, covering the resin bath would make it very difficult to monitor the wetting of the reinforcement.

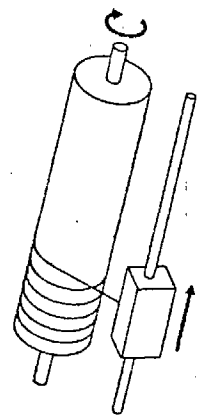
3.3.6 Filament Winding

Except where otherwise noted, this section is based upon a description by Como (1979). Filament winding is an increasingly popular method of manufacturing cylindrical products requiring high strength. In this process, continuous strands of reinforcement are impregnated with resin, wrapped around a rotating mandrel, and cured. Because of their high specific strength and relatively low cost, continuous glass fibers are most often used for the filaments; other fiber materials include graphite and aramid. The most common resins are epoxy, polyester, and vinyl ester. Low-viscosity resins are needed to allow resin to flow around each filament (Kober, 1981).

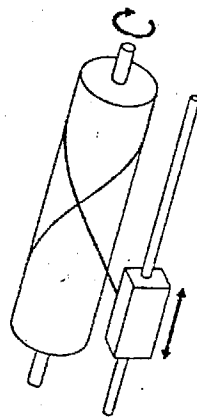
Figure 3.3-5 shows the three most common winding patterns. Note that in each case the mandrel spins but does not move longitudinally or laterally. Circumferential, or hoop, winding is used most often in conjunction with other winding patterns to increase hoop strength. Filaments are applied at right angles to the mandrel's axis of rotation. Helical winding is performed at winding angles of 15 to 85 degrees to the longitudinal axis of the mandrel; the angle determines the ratio of hoop to longitudinal strength. In polar winding, the angle to the longitudinal is from 0 to 15 degrees, and the reinforcing fibers are wrapped over the ends of the mandrel to prevent slippage. The different winding patterns may be used in combination to achieve desired strengths and shapes.

Mandrels are made of a wide variety of materials. To accelerate curing, hollow metal tubes are often used, permitting injection of steam through the center of the product. Mandrels which are to be removed are made in collapsible segments or of materials which can be dissolved or melted after the product is cured. In some cases, the mandrel remains inside the part as a liner or core.

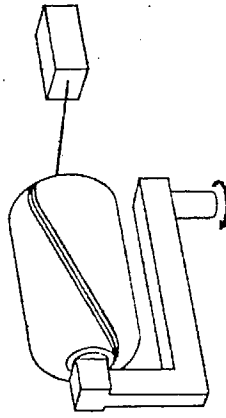
Machinery which combines filament winding with chopper spraying was recently described (Anon., 1978b). First, catalyzed resin is sprayed onto a



Circumferential Winding



Helical Winding



Polar Winding

Figure 3.3-5. Three Major Types of Filament Winding (Como, 1979).

mandrel which has been pre-coated with a release agent. A layer of chopped-strand roving and catalyzed resin is then applied. Filaments are wound onto the resin- and glass-coated surface until the desired thickness is achieved. A final surface coating of resin is then applied.

As noted above, filament winding is most suitable for products of relatively uniform cylindrical cross-section. Concave areas, which cause bridging of the filaments, and changes in curvature, which cause filament slippage, cannot be wound conveniently. The process is used mainly for the construction of tanks, pipes, and special pressure vessels. Recent applications include radio towers, radomes, helicopter blades, lift truck booms, automotive drive shafts, and flywheels for energy storage. A prototype railroad hopper car having a filament-wound polyester resin/fiberglass body shell was recently introduced (Anon., 1981e). The car, called a "Glass-hopper," has a greater payload per unit weight than does a conventional steel hopper car, and may be able to absorb and dissipate shock more readily.

The potential for organic vapor emissions from filament winding appears to be moderate. The requirement for low resin viscosity often implies the use of higher resin concentrations than with conventional laminating resins. Furthermore, catalysts are added to the resin in low enough concentrations that cure is delayed until after winding is completed (RCI, 1981); this delay could increase the availability of styrene for emission.

3.3.7 Closed Molding Processes

Bag Molding

In both vacuum bag and pressure molding, the part to be manufactured is first layed up by hand and/or spray techniques. In vacuum bag molding, the layup is covered with a film such as cellophane, polyvinyl alcohol, polyethylene or nylon. A vacuum is then drawn on the "bag" formed by the film and the layup. Atmospheric pressure on the film forces out entrapped air, improves resin distribution and glazes the surface. In pressure bag molding, the layup (which must be on a female mold) is covered with a rubber sheet, to which about 500 psi of pressure is applied. This process results in uniform physical characteristics and eliminates voids. In some cases either type of bagged assembly is placed in an autoclave and heated under pressure. This variant gives the product a higher density and allows use of a higher percent-

age of reinforcement materials. The emission potential of bag molding depends on the length of time the resin is exposed to the air before the bag is applied, since emissions after bagging would be negligible.

Resin Transfer Molding

Resin transfer molding (RTM) was virtually unknown 10 years ago and is used mainly in Europe (Anon., 1979a). In this process, continuous- or chopped-strand glass fiber mats are placed between the halves of a mold. After the mold is closed, catalyzed resin is injected and allowed to cure exothermically. The mold is then opened, and the finished part is removed. Sandwiches of polyurethane foam and polyester resin may also be made this way. A variation on the technique is to inject the resin at several points and to apply a strong vacuum at one end of the mold; resin flows more evenly through the mold, and voids are eliminated (Anon., 1979b). Vacuum-assisted resin transfer molding has been used in England to make racing yachts having foam cores. Since this process is entirely enclosed its emission potential is low.

3.3.8 New Processes

Application of Foamed Polyester

Foam systems for applying polyester resin to molds have been around for many years, but their use has been negligible. As will be discussed below, the chief problem has been the need--until recently--to store foaming agents at subzero temperatures. Now, however, "with the availability of new technology...and the climate of business increasingly receptive to the economies and other benefits feasible with foam, the stage appears set for a period of real growth" (Anon., 1980a). The process has been used since 1979 in a large bathtub/shower unit facility in Texas (Naitove, 1980).

Apparatus normally used for applying foamed plastics such as polyurethane can be modified for polyester foam use. The unsaturated polyester and the foaming agents are contained in separate canisters; when combined in a spray gun they react and evolve a gas which creates the foam.

The key ingredient in a polyester foam system is the foaming agent. Because of their potential threat to stratospheric ozone, fluorocarbons are not used. The first generation of polyester foaming agents were a family of azo compounds such as 2-tert-butylazo-5-methyl-2-hexanol, developed by Lucidol (a division of Pennwalt Corporation). These compounds decompose in the

presence of acidic groups in the polyester resin to form nitrogen gas (Wood, 1978b). Early versions of the agents were highly volatile and had to be stored at -18°C . Lucidol removed the product from the market in November 1980, after workers allegedly suffered nerve damage (Anon., 1981f). The latest Lucidol product is "Lucel-135," a methoxy azo compound which may be stored at room temperature and which has a pot life of a few days (Anon., 1980b). For room temperature molding the binary system consists of (1) polyester resin and Lucel 135 and (2) polyester resin and a two- to three-percent solution of phosphoric acid.

Another foaming agent has been developed by Whitney and Company of Stratham, New Hampshire. Their EMC-10 and EMC-20 compounds are bisphenyl-methyl formulations which react with MEKP to form CO_2 gas. The EMC-10 has a 40-hour pot life and can be pigmented. Standard spray equipment can be used (Wood, 1980).

A second polyester foam system is one developed by Tanner Chemical Company and the Polyceramic Development Center, both in Greenville, South Carolina. The "A" side consists of a one-to-one mixture of low-styrene polyester resin and calcium carbonate, plus a promoter (phenylethyl ethanolamine). The "B" side is a one-to-one mixture of aluminum trihydrate and "Cerfoam," a water-based inorganic polymer of proprietary formulation, plus benzoyl peroxide catalyst. Two parts of A are combined with one part of B via a conventional spray gun fitted with a glass chopper. Acids in the Cerfoam react with the CaCO_3 , releasing CO_2 gas, which produces the foam. During the exothermic reaction, a "ceramic cure" takes place, locking the water within the Cerfoam matrix (Anon., 1980c; Sels, 1981).

Light Curing of Resins

This relatively new technique uses visible light to convert a catalyst, which is added to polyester resin by the manufacturer, to a free radical. According to the developers of the technique (Dixon et al., 1977), resins gel and cure from the outside in. Since the outer layer cures within 10 to 15 seconds, styrene is trapped within the resin and emissions are reduced. Resins used in this process contain about 50 percent styrene, and cannot be pigmented (Lane, 1981). Xenon lamps designed to emit a specific wavelength to which the catalyst system is sensitive have been developed. The process has been used so far in conjunction with filament winding of pipes.

3.4 REGULATORY FRAMEWORK

3.4.1 Federal Regulation and Policy

The U.S. Environmental Protection Agency (EPA) has no New Source Performance Standards (NSPS) for the reinforced plastics fabrication industry and no regulatory measures are currently being considered (Crumpler, 1980). The EPA's Office of Air Quality Planning and Standards recently sponsored a screening study to determine whether NSPS should be set for the fiberglass manufacturing industry, but neither that study nor the regulations tentatively being considered have any bearing upon polyester resin/fiberglass fabrication (Telander, 1980).

3.4.2 State Regulations

Under the Clean Air Act Amendments of 1977, each state is to formulate and receive EPA approval for a State Implementation Plan (SIP) for preventing significant deterioration of air quality where federal primary ambient air quality standards are currently met and for achieving the standards in current non-attainment areas. Activities and regulations relating to federal and state ambient standards generally fall within one of two arenas--Prevention of Significant Deterioration and Non-Attainment.

Prevention of Significant Deterioration

Under the Prevention of Significant Deterioration (PSD) provisions of the Clean Air Act, three classes of "clean air" areas were created, a clean air area being one in which the federal ambient standards for SO_2 , total suspended particulates carbon monoxide, NO_x , hydrocarbons and ozone are met. In each classification, air quality is permitted to deteriorate by a prescribed maximum increment above the baseline condition existing at the time of the first permit application in a clean air area. These increments must be shared by all present and future sources in and around each air quality control region.

Non-Attainment

Any air quality control region in which the federal ambient standards are violated is designated as a non-attainment area. Construction of new or modified facilities in these areas is governed by EPA's emission offset policy, unless the state's SIP is adequate to manage non-attainment

areas. Under this policy, major sources must meet the following requirements before a construction permit may be issued:

- Emissions from the proposed facility must be more than offset by reducing emissions from existing sources, resulting in a positive net air quality benefit and reasonable further progress toward attainment of the ambient standard. A portion of "excess" offset credit may be banked for future use by the applicant, but interpollutant tradeoffs are not permitted.
- The proposed facility must have the Lowest Achievable Emission Rate.
- Any other major sources within the state which are owned by the applicant must be in compliance with applicable emissions standards or compliance schedules.

The Lowest Achievable Emission Rate (LAER) is defined as (1) the most stringent achievable emission limitation for a source category found in any SIP or (2) the most stringent emission limitation achieved in practice (or which can be reasonably expected to occur in practice) for that source category. The most stringent of these options is applicable (Ember, 1978). Draft LAER's are currently circulating for comment.

3.4.3 Local District Regulations

All the California local air pollution control districts (APCDs) having polyester resin/fiberglass fabrication operations within their jurisdiction were contacted in order to determine the extent to which styrene emissions from these processes were regulated. Table 3.4-1 lists the districts and the individuals we contacted.

Most of the districts include styrene emissions under their organic solvent rules or under new source review (NSR) regulations. While styrene, as the cross-linking agent in the polymerization of polyester resin, is incorporated permanently in the resin structure, it also serves as a diluent. Inclusion of polyester resin/fiberglass fabrication in organic solvent regulations is therefore logical. Since, as will be discussed in the next chapter, unambiguous classification schemes for this source category are lacking, the organic solvent approach is perhaps appropriate, even for cases in which styrene is not used as a diluent. We have recommended that the ARB establish category of emission source (CES) numbers for the several polyester resin/fiberglass fabrication processes. (See Chapter 2.).

Table 3.4-1
CONTACTS WITH CALIFORNIA LOCAL AIR POLLUTION CONTROL DISTRICTS
WHERE POLYESTER RESIN/FIBERGLASS OPERATIONS CAN BE FOUND

Local Air Pollution Control District	Name of Contact
Fresno County	Charles Maskel Air Pollution Engineer
Glenn County	Ed Romano
Kern County	Leon Hebertson, M.D. Air Pollution Control Officer
Madera County	Bill Stork
Merced County	Richard Wachs Air Pollution Engineer
Monterey Bay Unified ^a	Ed Kindig Air Pollution Engineer
Northern Sonoma County	Michael Tolmasoff Air Pollution Control Officer
Placer County	Kenneth Selover Air Pollution Control Officer
Sacramento County	Bruce Nixon Air Pollution Engineer
San Joaquin County	Mr. Grewall
San Luis Obispo County	Robert Carr Asst. Air Pollution Control Officer
Shasta County	Dale Watson Deputy Air Pollution Control Officer
Sutter County	Alfred Perrin, Jr. Air Pollution Control Officer
Tehama County	Donald Hill Air Pollution Control Officer
Tulare County	Mr. Johnson

Table 3.4-1
CONTACTS WITH CALIFORNIA LOCAL AIR POLLUTION CONTROL DISTRICTS
WHERE POLYESTER RESIN/FIBERGLASS OPERATIONS CAN BE FOUND
(continued)

Local Air Pollution Control District	Name of Contact
Ventura County	Jan Bush Air Pollution Control Officer
Yolo-Solano	Mr. Koslow
Yuba County	Dave McBride
Bay Area	Bill deBoisblanc Chief of New Source Review
South Coast	
San Diego County	Ray Skoff Associate Air Pollution Control Engineer
Santa Barbara County	Doug Grapple Air Pollution Engineer

^a Includes Monterey, Santa Cruz and San Benito Counties.

None of the 22 affected local APCDs has specific emission rate regulations governing the release of styrene from polyester resin/fiberglass manufacture. However, both the Bay Area Air Quality Management District (BAAQMD) and the Shasta County APCD allude to the use of polyester resin in reinforced plastic manufacturing processes in their organic solvent regulations (BAAQMD Regulation 8-4-111, Shasta County Rule 3:4, b.,3.). The Bay Area regulation exempts users of polyester resins if such use, after application, does not result in the emission of organic gases in excess of 6 percent by weight of the resin. Shasta County also grants exemptions for users of polyester resin. Here, the maximum percent loss of organic gas from gel coat and laminating resin processes may not exceed 22 and 8 percent by weight, respectively. This particular exemption expired as of January 1, 1982 and there are presently no plans to update the old rule (Watson, 1982).

New source review regulations were the only other potentially applicable regulations cited by local air pollution officials. For example, in order to comply with non-attainment regulatory obligations, Sacramento County APCD's NSR rules provide that "best available control technology" (BACT) must be used if VOC emissions are between 150 and 250 pounds per day. If the operation emits more than 250 pounds per day VOC, then pollution offsets must be granted to surrounding air pollution sources (Nixon, 1982).

The Monterey Bay Unified APCD's NSR regulation is essentially the same except that if a new or modified operation emits more than 200 pounds per day, then emission offsets and "lowest achievable emission rates" (LAER) apply (Kindig, 1982). The remaining districts located in non-attainment areas either use slight variations of the above NSR scheme or use guidelines such as the old Los Angeles County organic solvent use code, Rule 66.

3.5 REFERENCES

Anon. 1970. "Reinforced plastics," Encyclopedia of polymer science and technology, Interscience Publishers, New York 12:1-41.

Anon. 1978a. "Clairty, cure control, fast action: all from new additive for polyester," Modern Plastics 55(9):22.

Anon. 1978b. "New chop/hoop winder speeds production of RP cylinders," Modern Plastics 55(5):22.

- Anon. 1979a. "Resin injection builds steam in Europe," Plastics World 37(5):24,26.
- Anon. 1979b. "Resin injection for FRP tackles custom marine markets," Plastics World 37(4):23.
- Anon. 1980a. "Growth coming for polyester foam," Modern Plastics 57(11):16,18.
- Anon. 1980b. "Blowing agents," Modern Plastics 57(9): 59,62-63.
- Anon. 1980c. "Filler/foam approach to RP cost control," Modern Plastics 57(8):16.
- Anon. 1981a. "Resinforced plastics expect moderate recovery," Chemical and Engineering News 59(8):17.
- Anon. 1981b. "Facts and figures for the chemical industry," Chemical and Engineering News 59(23):30-83.
- Anon. 1981c. "Owens-Corning: boom for reinforced plastics," Chemical and Engineering News 59(21):16.
- Anon. 1981d. "Key polymers: polyesters," Chemical and Engineering News 59(39):17.
- Anon. 1981e. "Glass fiber-reinforced hopper car unveiled," Chemical and Engineering News 59(14):36.
- Anon. 1981f. "Foaming agents for polyester developed," Chemical and Engineering News 59(10):30-31.
- Atkinson, R., K.R. Darnall et al. 1981. "Kinetics and mechanisms of the reaction of the hydroxyl radical with organic compounds in the gas phase," Statewide Air Pollution Research Center and Department of Chemistry, University of California, Riverside, California. (Chemical data printout provided by California Air Resources Board.)
- Avery, J.A. 1979. "Thermoplastic polyester: PBT," Modern plastics encyclopedia 1979-1980, McGraw-Hill Inc., New York, pp. 49-50.
- Boenig, H.V. 1964. Unsaturated polyesters. Elsevier, Amsterdam. (Cited in Brighton et al. 1979).
- Brighton, C.A., G. Pritchard and G.A. Skinner. 1979. Styrene polymers: technology and environmental aspects. Applied Science Publishers, Ltd., London, 294p.
- Byron, D.A. 1980. "Southland's boat sales slip away," Los Angeles Times (17 December), Part I, pp. 1,20.
- Como, F.W. 1979. "Filament winding," Modern plastics encyclopedia 1979-1980, McGraw-Hill Inc., New York, pp. 375-376.

Crumpler, Dennis, U.S. Environmental Protection Agency, Office of Air Quality Planning and Management, Emissions Standards and Engineering Division, Research Triangle Park, North Carolina. Personal Communication (8 February 1980).

Czarnomski, T.J. 1979. "Unsaturated polyester," Modern plastics encyclopedia 1979-1980, McGraw-Hill Inc., New York, pp. 55-56,58.

Dixon, B.G., D.M. Longenecker and G.G. Greth. 1977. "The curing of unsaturated polyester resins with visible light." Presented at the 32nd Annual Technical Conference of the Reinforced Plastics/Composites Institute, Section 5-D.

Edwards, H.R. 1979. "Variables influencing the performance of gel-coated composites," Modern Plastics 56(8):49,54,56-57.

Ember, L.R. 1978. "EPA's emission offset policy," Environmental Science and Technology 12(9):1007,1008,1011.

Ewald, G.W. 1979. "Pultrusion," Modern plastics encyclopedia 1979-1980. McGraw-Hill Inc., New York, pp. 379-381.

Gallagher, R.B. and V.R. Kamath. 1978. "Organic peroxides review. 1. Room temperature cure of polyester resin systems," Plastic Design and Processing 18(7):38-42.

Hoshika, Y. 1977. "Gas chromatographic determination of styrene as its dibromide," Journal of Chromatography 136(1):95.

Kent, J.A. (Ed.). 1974. Riegel's handbook of industrial chemistry, Seventh edition, Van Nostrand Reinhold Company, New York, pp. 280-282.

Kindig, Ed, Air Pollution Engineer, Monterey Bay Unified Air Pollution Control District. Personal communication (21 January 1982).

Kirshenbaum, G.S. and J.M. Rhodes, 1979. "Thermoplastic polyester: PET." Modern plastics encyclopedia 1979-1980, McGraw-Hill Inc., New York, pp. 50,52.

Kober, J.F. 1980. "The filament winding market-a modern day review," Proceedings of the 3rd Biennial Technical Conference on Corrosion Resistant Structures and Construction, Long Beach, California, 15-17 September 1981 Western Section, Reinforced Plastics/Composites Institute, pp. 32-36.

Lane, Larry, ICI Americas, Inc., Wilmington, Delaware. Personal communication (24 February 1981).

Lichtenberg, D.W. 1979. "Reinforced thermosets," Modern plastics encyclopedia 1979-1980, McGraw-Hill Inc., New York, pp. 55-56,58.

Lucidol-Pennwalt. 1981. "Standard MEK peroxides." Product bulletin, Buffalo, New York.

Martin, J.D. 1979. "Putrusion: the other process," Plastics Engineering 35(3):53-57.

May, J. 1966. "Solvent odor thresholds for the evaluation of solvent odors in the atmosphere," Staub-Reinhalte 26(9):385-389.

Naitove, M.H. 1980. "With polyester foam, the payoff is productivity," Plastics Technology 26(3): 79-83.

Neligan, R.E., M.J. Leonard, and R.J. Bryan. 1965. "The gas chromatographic determination of aromatic hydrocarbons in the atmosphere," American Chemical Society, Division of Water, Air Waste Chemistry Preprints 5(2):118-121.

Nelson, D.L. 1978. "Introducing low-cost dicyclopentadiene into unsaturated polyester resins," Modern Plastics 55(9):92-93.

Nixon, Bruce, Air Pollution Engineer, Sacramento County Air Pollution Control District. Personal communication (21 January 1982).

Reichhold Chemicals, Inc. 1981. "Polylite polyester resins and Corrolite vinyl ester resins for corrosion-resistant applications," Product Brochure CR 03.

Rich, R.P. 1979. "Thermoplastic copolyester," Modern plastics encyclopedia, McGraw-Hill, Inc., New York, p. 55.

Santodonato, J., W.M. Meylan et al. 1980. Investigation of selected potential environmental contaminants: styrene, ethylbenzene, and related compounds. Prepared by Syracuse Research Corporation for U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., EPA-560/11-80-018 (NTIS: PB81-102659).

Sels, J., Polyceramic Development Center, Greenville, South Carolina. Telephone conversation (23 February 1981).

Shreve, R.N. and J.A. Brink, Jr. 1977. Chemical process industries, 4th edition, McGraw-Hill Book Company, New York, p. 572.

Sing, B. 1981. "Boat industry faces troubled upturn," Los Angeles Times (10 August), Part VI, pp. 1-2.

Smith, H.C. and A. Hochstettler. 1969. "Determination of odor thresholds in air using carbon-14 labeled compounds to monitor concentrations," Environmental Science and Technology 3(2): 169-170.

Telander, Jeff, U.S. Environmental Protection Agency, Office of Air Quality Planning and Management, Emissions Standards and Engineering Division, Research Triangle Park, North Carolina. Personal communication (8 February 1980).

Verschueren, K. 1977. Handbook of environmental data on organic chemicals, Van Nostrand Reinhold Company, New York.

Watson, Dale, Deputy Air Pollution Control Officer, Shasta County Air Pollution Control District. Personal Communication (20 January 1982).

White, J.S. 1979. "Continuous RP laminating," Modern plastics encyclopedia 1979-1980, McGraw-Hill, Inc., New York, pp. 374-375.

Wood, A.S. 1978. "Pultrusion comes on as a new process for cost-saving mass production," Modern Plastics 55(5):50-52.

Wood, A.S. 1978b. "The action starts in polyester foam," Modern Plastics 55(6):37-39.

Wood, A.S. 1980. "Polyester foam -- much of it reinforced -- set for big commercial growth," Modern Plastics 57(12):46-47.

SURVEY OF POLYESTER RESIN USE IN CALIFORNIA

The objective of this part of the project was to characterize the polyester resin/fiberglass industry in California. In order to estimate emissions and formulate control strategies, we needed to know how many plants there were, where they were located, how much polyester resin they consumed, and what production and control processes they used. We therefore conducted a survey of the industry, and, from the information obtained, we constructed an emission inventory. This chapter describes our survey methods and results.

4.1 SURVEY METHODS

4.1.1 Sources of Names of Polyester Resin Users

Before this study was conducted, no comprehensive list of polyester resin users in California was known to exist. Since polyester resin is used in a wide variety of industries, use of the resin could not be unambiguously associated with any Standard Industrial Classification (SIC) code. Furthermore, SIC codes under which many polyester resin users fall are applicable to an equal or greater number of non-users. Those SIC codes most likely to include the types of firms under consideration were 3079 (Miscellaneous Plastics Products) and 3732 (Ship and Boat Building and Repairing). Sources of names of polyester resin users included the following.

California Manufacturers Register

Previous experience had shown the California Manufacturers Register (CMA, 1980) to be useful in identifying companies under given SIC codes. We therefore began our survey by reviewing the listings in this publication under codes 3079 and 3732. Since the products of each firm are reported, we were able to eliminate from consideration those which were obviously not polyester resin users. Nevertheless, only about one-third of the companies remaining after this initial screening turned out, upon being surveyed, to be users. Because inclusion in the California Manufacturers Register is voluntary, a large number of polyester resin users -- including some very large ones -- were not listed. Roughly 100 companies were identified through this source.

Statewide Emission Inventory

Early in the project, we asked the ARB's Stationary Source Emissions Division to run a search on the Emission Data System (EDS), using SIC codes 3079 and 3732, along with the U.S. Environmental Protection Agency's Source Classification Code 3-08-007-99 ("Fabricated Plastic Products, Other/Not Classified") to identify possible polyester resin users. The search identified 87 firms, some of which had already been found through the California Manufacturers Register. Three problems with using the inventory were encountered. First, 34 of the firms were, according to the process descriptions reported by the EIS, not polyester resin users. Second, several firms had gone out of business since 1977, when the inventory had last been updated. Finally, since the inventory generally contains firms having certain minimum emission rates of criteria pollutants, many small polyester resin users were not included. In spite of these problems, the inventory search was useful in providing the names of many of the major users, especially in Los Angeles and Orange Counties.

The EDS printout included Source Classification Codes for each of the processes contributing to hydrocarbon emissions. As a set of these may be useful in future studies of this industry, we list them in Table 4.1-1. It is clear from the table that there is currently no unambiguous way to classify sources of emissions from polyester resin/fiberglass fabrication. Codes for surface coating and solvent evaporation are frequently used, although the pollutants of interest are generally an integral part of the manufactured product. The codes beginning with 3-05-12 are more properly associated with the manufacture of wool-type glass fiber materials, not reinforced plastics (USEPA, 1981), yet they have been used for firms which make the latter. The classification problem is discussed further in Chapter 2, Recommendations.

San Diego County Air Pollution Control District

At our request, the San Diego County Air Pollution Control District ran a search of its own stationary source emission inventory. Most of the 25 firms identified turned out to be polyester resin users. Relevant characteristics of each plant, including hydrocarbon emission estimates, were included in the computer printout.

Table 4.1-1

SOURCE CLASSIFICATION CODES (SCC) ASSOCIATED WITH
POLYESTER RESIN/FIBERGLASS OPERATIONS

SCC NO.	Standard Definition	Description in Statewide Emission Inventory
3-05-012-04	Fiberglass mfg: forming line	None
3-05-012-99	Fiberglass mfg: other/not classified	Air-cured fiberglass, fiberglass bath features, fiberglass spray booth
4-02-001-01	Surface coating-paint: general	Fiberglass resin spray
4-02-003-01	Surface coating-varnish/shellac: general	Gel coat, polyester resin, spray booth
4-02-005-01	Surface coating-enamel: general	None
4-02-005-49	Surface coating-enamel: solvent general	Spray booth
4-02-007-01	Surface coating-adhesive: general	None
4-02-008-03	Surface coating-coating oven: baked >175°	Coating-drying, laminated board processing
4-02-009-02	Surface coating-solvent: acetone	Gelcoat, resin
4-02-999-99	Surface coating-solvent: to be specified	Gelcoat, gelcoat spray, polyester spray
4-90-999-99	Miscellaneous HC evaporation: to be specified	Fiberglass, gelcoat, resin

Bay Area Air Quality Management District

On 23 July 1980 SAI staff visited the Bay Area Air Quality Management District (BAAQMD) office in San Francisco and reviewed a list of permit holders. BAAQMD staff pointed out which of the holders were known to be polyester resin users. Names and addresses of 40 plants were obtained. Since this particular list had not been updated in several years, 8 of the firms identified turned out to be defunct, and 12 were not actually polyester resin users.

Shasta County Air Pollution Control District (SCAPCD)

While discussing styrene evaporation tests performed by the Shasta County Air Pollution Control District (see Section 5.1.4), we learned from SCAPCD staff that the agency had compiled a list of polyester resin users within its jurisdiction. At our request, the SCAPCD sent us names, addresses, estimated resin use rates, and estimated emission rates for seven firms (Burns, 1980).

Other Local Air Pollution Control Districts

When the survey was about half completed, it appeared that 24 of California's 58 counties had no polyester resin users. To be sure that no users were missed, we sent a cover letter and questionnaire to the corresponding agencies (see Appendix A). The exercise resulted in the identification of 6 additional firms, as well as confirmation of the nonuse of polyester resin in 21 counties.

Society of the Plastics Industry

Local representatives of the Society of the Plastics Industry, Inc. (SPI) furnished us with the 1980 Membership Directory and Buyers Guide (SPI, 1980), as well as assorted other materials on polyester resin manufacturers and users. While the directory contained only a few manufacturers not listed elsewhere, it proved valuable in our survey of resin formulators (see Section 4.1.3).

Telephone Directory

After all of the above mentioned sources of information had been exhausted, it appeared to us that a significant number of polyester resin users had still not been identified. While, as discussed elsewhere in this

report, the number of users and the total resin use rate in California are unknown, our tentative totals were lower than those estimated by the air pollution control agencies and resin manufacturers with whom we discussed the matter. We therefore turned to the telephone directories of all major metropolitan areas in California. Names of putative polyester resin users were chosen from among the listings under "Fiberglass Fabricators," "Boat Building and Repairing," "Surfboards," "Marble-Synthetic," and "Tanks." Though tedious, this search proved highly productive.

Other Information Sources

About a dozen users were identified through miscellaneous means. A major resin manufacturer named two of its largest customers. Some plants told us of branch facilities of which we had been unaware. One of the largest users in the state was not listed in any of the sources mentioned here; the principal investigator happened to drive past it one day.

4.1.2 Keeping Track of Firms in Survey

Since almost 950 firms were surveyed, it was necessary to set up a system to keep track of the status of knowledge on each company. First, 3 x 5 inch cards containing preliminary information such as name, address, phone number, and SIC code (if known) were filled out for each putative user. Each company was identified with a unique number, which was later used on questionnaire forms and/or data coding sheets. Figure 4.1-1 shows a typical index card. The name, address and phone number of the company has been deleted to preserve confidentiality. The meaning of the various notations on the card are explained in the figure. During the survey, cards were stored alphabetically in three groups: non-users, users for which data were complete, and users for which data were lacking. Meanwhile, a survey status register was set up to keep track of all the firms. Companies were listed by survey identification number. For each polyester resin user, we recorded the number of the data coding sheet on which it appeared, the date on which information was received, and whether the data had been stored on floppy disk.

4.1.3 Data Acquisition

In conducting our survey, we gave the highest priority to data which could be used to (1) characterize the industry, (2) choose emission test sites, (3) estimate organic vapor emissions and (4) recommend emission control

strategies. We therefore limited our survey to what we considered to be the most important items. These were:

- Type of product(s) manufactured
- Fabrication process(es)
- Polyester resin use rate
- Gel coat use rate
- Type of cross-linking agent (monomer)
- Percent of cross-linking agent in resin and gel coat
- Type of catalyst
- Whether a vapor suppressant is used
- Operating schedule
- Emission control system (if any)
- Means of venting vapors to the atmosphere

All but a few of the potential polyester resin users were sent a letter explaining the purpose of the survey and assuring that firm specific information would be furnished only to the ARB. Figures 4.1-2 and 4.1-3 show the letters sent to firms which were contacted by telephone and written questionnaire, respectively. The handful of firms not initially contacted in writing were nevertheless explained ARB's policies regarding confidentiality.

In general, firms which were in the 213 and 714 telephone area codes were interviewed by telephone, while the rest were sent questionnaires. Some companies refused to answer questions by telephone, but did respond in writing. Because we were to establish as complete an inventory of polyester resin users as possible, all firms which did not return questionnaires were later telephoned. In some cases, as many as ten attempts were necessary before an interview could be conducted.

Figure 4.1-4 shows the written questionnaire used in the survey. The same set of questions was used in the telephone interviews, although in many cases considerably more detailed information was obtained. During the telephone interviews, the caller entered certain data items immediately on a coding form, which is discussed below. Resin and gel coat use rates were recorded separately in the form stated by the interviewee (e.g. gallons per day



Dear Sir:

Science Applications, Inc. (SAI) is under contract to the Research Division of the California State Air Resources Board (ARB) to investigate techniques to control organic gas emissions from operations where polyester resin is used in California. The objectives of our research are (1) to estimate emissions (principally styrene) by type of operation and by county and (2) to survey present and developing control technology. We are particularly interested in control strategies which minimize the financial burden upon small businesses.

In order to obtain basic information on polyester resin use, styrene emissions, and control technology in California, we are conducting a telephone survey of approximately 600 firms. Your firm was selected from a list of manufacturers of products under Standard Industrial Classification (SIC) Codes 3079 (Miscellaneous Plastics Products) and 3732 (Boat Building and Repairing). Either I or another SAI staff scientist will be calling you within the next three weeks to ask you about the following aspects of your operation:

- (1) Whether you use polyester resin
- (2) Types of products produced
- (3) Resin use rate (e.g., drums per day)
- (4) Fabrication process (hand layup, chopper gun, filament winding, etc.)
- (5) Percentage of styrene in resin
- (6) Vapor emissions control techniques (Including use of suppressants in the resin.)

This request for data is a formal one made by the ARB pursuant to Section 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code, which authorize ARB, or its duly appointed representative, to require the submission of air pollution related information from owners and operators of air pollution emission sources. We are required by the ARB to furnish them with the name of each polyester resin user, along with our estimate of organic vapor emissions. Polyester resin use data will remain confidential, as will information on proprietary

Figure 4.1-2. Letter Sent in Advance of Telephone Interview

processes and costs. If this arrangement is unsatisfactory to you please inform our caller.

The ARB Research Contracts Monitor for this project is Mr. Joseph Pantalone, whose telephone number is (916) 323-1535. Our contract number is A9-120-30.

Thank you for assisting us in this survey.

Sincerely,

SCIENCE APPLICATIONS, INC.

Michael B. Rogozen, D. Env.
Principal Investigator

MBR/vm

Figure 4.1-2 (Ctd). Letter Sent in Advance of Telephone Interview



Dear Sir:

Science Applications, Inc. (SAI) is under contract to the Research Division of the California State Air Resources Board (ARB) to investigate techniques to control organic gas emissions from operations where polyester resin is used in California. The objectives of our research are (1) to estimate emissions (principally styrene) by type of operation and by county and (2) to survey present and developing control technology. We are particularly interested in control strategies which minimize the financial burden upon small business.

In order to obtain basic information on polyester resin use, styrene emissions, and control technology in California, we are conducting a survey of approximately 1,000 firms. Your firm was selected from a list of manufacturers of products under Standard Industrial Classification (SIC) Codes 3079 (Miscellaneous Plastics Products) and 3732 (Boat Building Repairing). Attached is a set of questions that we have been asking all identified users. Please fill in the blanks and return the questionnaire in the enclosed stamped envelope. We would appreciate it if you could respond within two weeks. The form should be returned even if you are not a user; simply check "no" in Item 1.

This request for data is a formal one made by the ARB pursuant to Section 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code which authorize ARB, or its duly appointed representative, to require the submission of air pollution related information from owners and operators of air pollution emission sources.

We understand that many firms are reluctant to furnish information which they consider to be privileged. The ARB has informed us that actual air pollution emission data cannot be classified as trade secrets, but other data such as privileged processes, costs, formulas, etc., may be eligible for such treatment. The information provided in the questionnaire can be released to the public upon request unless you request trade secret classification in writing (in accordance with the California Public Records Act, Government Code Section 6250 et seq.). All such requests must be accompanied by an adequate justification for the trade secret designation, which should be as detailed as possible without disclosing the trade secret.

Figure 4.1-3. Letter Accompanying Written Questionnaires

Science Applications, Inc. 1801 Avenue of the Stars, Suite 1205, Los Angeles, CA 90067 (213) 553-2705

Other SAI Offices: Albuquerque, Atlanta, Chicago, Dayton, Denver, Hunt 62 Angeles, Oak Ridge, San Diego, San Francisco, Tucson, and Washington D.C.

Information supplied to ARB which is designated as a trade secret will be kept confidential, although such information may be forwarded to the U.S. Environmental Protection Agency, which protects trade secrets in accordance with federal law. Please note that SAI has formally agreed with the ARB to protect the disclosures of trade secrets to others. Further information on ARB policy may be obtained from the ARB research contract monitor, Mr. Joseph Pantalone, whose telephone number is (916) 323-1535. Our contract number is A9-120-30.

My assistant, Mr. Alan Miller, and I will be happy to answer any questions about the questionnaire and our study. We may be reached at the address and phone number listed at the bottom of the first page of this letter.

Thank you very much for assisting us in this survey.

Sincerely,

SCIENCE APPLICATIONS, INC.

A handwritten signature in cursive script that reads "Michael B. Rogozen". The signature is written in dark ink and is positioned above the printed name.

Michael B. Rogozen, D.Env.
Principal Investigator

/e

Enc.

Figure 4.1-3 (Ctd). Letter Accompanying Written Questionnaires.

SCIENCE APPLICATIONS, INC.
POLYESTER RESIN USER QUESTIONNAIRE

Firm No. _____

Date _____

1. Do you use polyester resin? Yes _____ No _____
2. What types of products do you make? _____

3. Which fabrication processes do you use:
_____ Hand lay up _____ Filament winding
_____ Spray lay up _____ Pultrusion
_____ Bag molding _____ Closed injection molding
_____ Continuous lamination _____ Other (specify); _____
4. Do you apply a separate gel coat? Yes _____ No _____
5. How much resin do you use: (drums/day, gal/week etc.)? _____

6. Is styrene the cross-linking agent? Yes _____ No _____
If not, what is? _____
7. What percentage of the resin consists of styrene? _____
8. Is MEK peroxide the catalyst? Yes _____ No _____*
9. Does the resin come with a suppressant mixed in? Yes _____ No _____
(If uncertain, please specify the manufacturer and type): _____

10. Is the suppressant also in the gel coat? Yes _____ No _____
11. Do you operate 8 hrs/day, 5 days/wk, 52 wks/yr? Yes _____ No _____
(If you have a different schedule, please specify): _____

* If not, what is? _____

12. What method(s) do you use to control styrene vapors in the plant? Where are vents located? Is there ducting to one or two exhaust points? _____

13. On a separate sheet, please note the name, address and phone number of any other polyester resin user(s) affiliated with your company.
14. How much gel coat do you use? What percentage of the gel coat consists of styrene? _____

Figure 4.1-4 (Ctd). Polyester Resin Use Questionnaire

or drums per week) and later converted into lb/year. Descriptions of control and venting systems were also noted separately.

It became apparent early in the survey that over half of the polyester resin users did not know the percentage of styrene (or other monomer) in their resin and gel coat. Most of them were, however, able to give us the names of the resin and gel coat manufacturers. As is discussed in Section 4.2.2, we decided to use product data for cases in which the actual monomer content was known. A telephone survey of the 13 manufacturers of polyester resin and/or gel coat accounting for the overwhelming majority of polyester resin use in California was therefore made.

4.2 EMISSION INVENTORY DATA MANAGEMENT

4.2.1 Initial Coding of Survey Data

To aid in the computer processing of survey results, we set up a system to code the data obtained through the telephone interviews and written questionnaires. Table 4.2-1 shows how data on production processes and resin use were coded. All artificial marble manufacturing process were coded with a 7, even though they could also be considered to be hand layup. Most of the information was coded immediately upon receipt of the written questionnaires or during the telephone interviews. Because resin and gel coat use were expressed in so many different types of units, however, we made the conversion to pounds per year before coding. Many of the firms contacted did not know the percentage of styrene in their resin and/or gel coat, but did know the name of the resin manufacturer. In those cases, we used the percentages obtained in our survey of 13 formulators.

Table 4.2-2 shows the codes used to characterize the pathways by which organic vapors are emitted to the atmosphere. The main purpose of this classification was to identify plants meeting one of our criteria for testing, i.e., those whose emissions were channeled through point emission sources. "Passive" pathways were defined as those through which vapors are emitted by diffusion and convection or through natural ventilation. Examples are open windows and skylights. In all other cases (except outdoor operation), fans or blowers move air from the workplace to the outdoors. Where more than one emission pathway was reported, firms were asked to identify the one corresponding to the greater part of the emissions.

Table 4.2-1

POLYESTER RESIN/FIBERGLASS INDUSTRY SURVEY CODES

CONTACT

- 0 Not called
- 1 Interviewed
- 2 Out of business/moved
- 3 Refused to answer
- 4 Sent written reply
- 5 Not a manufacturing plant
- 6 Same as other plant
- 7 Data from local APCD

RESIN USER

- 0 No
- 1 Yes
- 9 Don't know

GEL COAT USER

- 0 No
- 1 Yes
- 9 Don't know

PROCESS TYPE

- 0 Don't know
- 1 Hand layup
- 2 Spray layup
- 3 Bag molding
- 4 Continuous lamination
- 5 Filament winding
- 6 Pultrusion
- 7 Marble
- 8 Matched metal molding
- 9 Other (specify)

CROSS-LINKING AGENT

- 1 Styrene
- 2 Vinyl toluene
- 3 Methyl methacrylate
- 4 Other (specify)

CATALYST

- 0 Don't know
- 1 MEK peroxide (MEKP)
- 2 Benzoyl peroxide (BP)
- 3 Other (specify)
- 4 BP in resin, MEKP in gel coat
- 5 Cumene hydroperoxide
- 6 2,4-pentanedione peroxide
- 7 MEKP, sometimes BP

VAPOR SUPPRESSANT

- 0 Not used
- 1 Used, but not in gel coat
- 2 Used in resin and gel coat
- 3 Used in resin; no gel coat used
- 9 Don't know

Table 4.2-2
EMISSION PATHWAYS CODES

Code	Description
1	Outdoor operation or home repair
2	Ducts: spray booths to wall outlet
3	Ducts: spray booths to roof outlet
4	Ducts: general work area to wall outlet
5	Ducts: general work area to roof outlet
6	Forced air: ceiling vents only
7	Forced air: wall vents only
8	Forced air: wall and ceiling vents
9	Passive wall vents only
10	Passive ceiling vents only
11	Passive ceiling and wall vents
12	Ducts: general work area to wall <u>and</u> roof outlets
13	Unknown
14	Water curtain
15	Afterburner

Table 4.2-3
PRODUCT CODES

Code	Description
0	Unknown
1	Boats
2	Marble
3	Auto, motorcycle, truck, aircraft or RV parts
4	Bathtubs, sinks etc. (not marble or spas or hot tubs)
5	Tanks, boxes, etc. gondolas
6	Furniture
7	Pipes, ducts, flues
8	General fiberglass, including custom
9	Radomes
10	Panels, laminates in general
11	Electronics
12	Helmets, sporting goods
13	Swimming pools and equipment mfg
14	Repairs at homes, etc.
15	Spas, hot tubs, jacuzzis
16	Pultruded rods, antennae etc.
17	Surfboards

In the original survey design, it was considered useful to learn the SIC code of each firm. As mentioned in Section 4.1.1, however, SIC codes constitute a poor guide to this industry. In order to analyze our survey data in a more meaningful way, we defined the set of product codes shown in Table 4.2-3. Most of the categories are self-explanatory. "General" includes firms which make prototype molds or which manufacture a wide variety of short-run products. "Tanks, Containers" includes large storage tanks, gondolas, cargo containers, and small boxes, except for electronics enclosures. Several firms manufacture both tanks and ductwork; these were placed in the "Pipes, Ducts" category. Only firms which specifically reported manufacturing synthetic marble were placed in that category; it is possible that some placed in the "Bathroom Fixtures" category may also be marble manufacturers. "On-Site Repairs" refers to services which resurface swimming pools, shower stalls, and other fiberglass items at the place of use.

4.2.2 Adjustments to Fill Data Gaps

An earnest effort was made to obtain all the desired data from each polyester resin user in the state. In a large number of cases, follow-up calls were made to get information omitted from the questionnaire or not reported in the telephone interview. Nevertheless, many data gaps remained at the end of the survey. The most important types of missing information were gel coat use rate, percentage of cross-linking agent in the laminating or casting resin, and percentage of styrene in the gel coat. Although about one quarter of the firms are deficient in one of these data categories, they represent only a tiny fraction of the polyester resin use in California. Errors in estimating values for the missing parameters would therefore not be expected to have much of an effect upon industry-wide totals and averages. Missing data were synthesized in the following ways.

Gel Coat Use Rate

A review of the survey data showed three important relationships between use of laminating resin and gel coat. First, gel coat is almost never used in connection with certain fiberglass production processes, including continuous lamination and pultrusion. Second, certain products, such as surfboards, are usually not made with a gel coat layer. Finally, the mean ratio between laminating resin use and gel coat use is not significantly different for different final products. We therefore synthesized a gel coat

Table 4.2-4

RATIO BETWEEN GEL COAT USE AND LAMINATING OR
CASTING RESIN USE, BY TYPE OF PRODUCT

Product Code ^a	Number of Cases	Mean Value of Ratio	Standard Deviation	t-value ^b
0	25	0.143	0.218	-0.558
1	56	0.138	0.183	-0.632
2	46	0.103	0.264	0.510
3	17	0.127	0.080	-0.156
4	7	0.190	0.095	-0.958
5	22	0.139	0.247	-0.434
6	5	0.082	0.114	0.871
7	5	0.018	0.029	1.174
8	22	0.132	0.133	-0.275
9	NA ^c	NA	NA	NA
10	8	0.018	0.051	1.482
11	5	0.171	0.152	-0.580
12	2	0.019	0.027	0.736
13	3	0.179	0.169	-0.524
14	4	0.200	0.245	-0.817
15	7	0.122	0.078	-0.028
16	5	0.039	0.054	0.932
17	NA	NA	NA	NA

^aCodes are defined in Table 4.2-3

^bFor hypothesis that mean ratio for a given product code is different from mean ratio for all cases; to be significant at the 0.05 level, $|t \text{ value}| > 1.960$.

^cNA = Not applicable.

use rate where needed by multiplying the laminating resin use rate by the average resin/gel coat factor, which was 0.12 ± 0.02 , or by zero if the process or product does not ordinarily use gel coat. (See Table 4.2-4).

Percentage of Cross-Linking Agent in the Resin and Gel Coat

Since the percentage of cross-linking agent in a polyester resin affects the latter's handling characteristics, it stands to reason that this parameter would vary from process to process. An analysis of all cases for which the cross-linking agent percentage was known showed that the percentage indeed was significantly different for certain processes. Table 4.2-4 shows the values used to supplant missing data.

4.2.3 Computerized Data Management System

Survey data were stored and analyzed with an Apple II microcomputer having 48K bytes of random access memory and a disk drive. To manage the data, a set of program modules were written in BASIC. Figure 4.2-1 shows the interrelationships between the programs and the data, with arrows showing the direction of information flow. Survey data were stored in two ways. First, a separate sequential text file, containing all the information obtained through the survey, was set up for each plant. Figure 4.2-2 shows how these files were arranged. In order to facilitate data analysis, we then created several data element files, each one containing values of one data element for all the firms. For example, one of these files consists of the resin use for each firm. The structure of the random access files is also shown in Figure 4.2-2. The following are brief descriptions.

- DATA INPUT -- This is an interactive program which requests each type of information and then stores it in random access memory. When all the data for given firm are entered, the program displays the data set and asks the user if all are correct. Erroneous data elements can be corrected immediately. At the user's command, the data set is then stored on disk. The name of the data file consists of the first 15 characters of the firm's name.

Table 4.2-5
RESIN STYRENE PERCENTAGES USED WHERE DATA WERE LACKING

Process Combination	Pct. Styrene in Resin
Hand layup alone	41.1
Hand layup, spray layup	42.7
Hand layup, spray layup, bag molding	40.0
Hand layup, spray layup, filament winding	43.1
Hand layup, bag molding	45.0
Hand layup, other	10.0
Spray layup alone	41.5
Spray layup, bag molding	25.0
Spray layup, filament winding	45.0
Continuous lamination alone	40.0
Filament winding alone	45.0

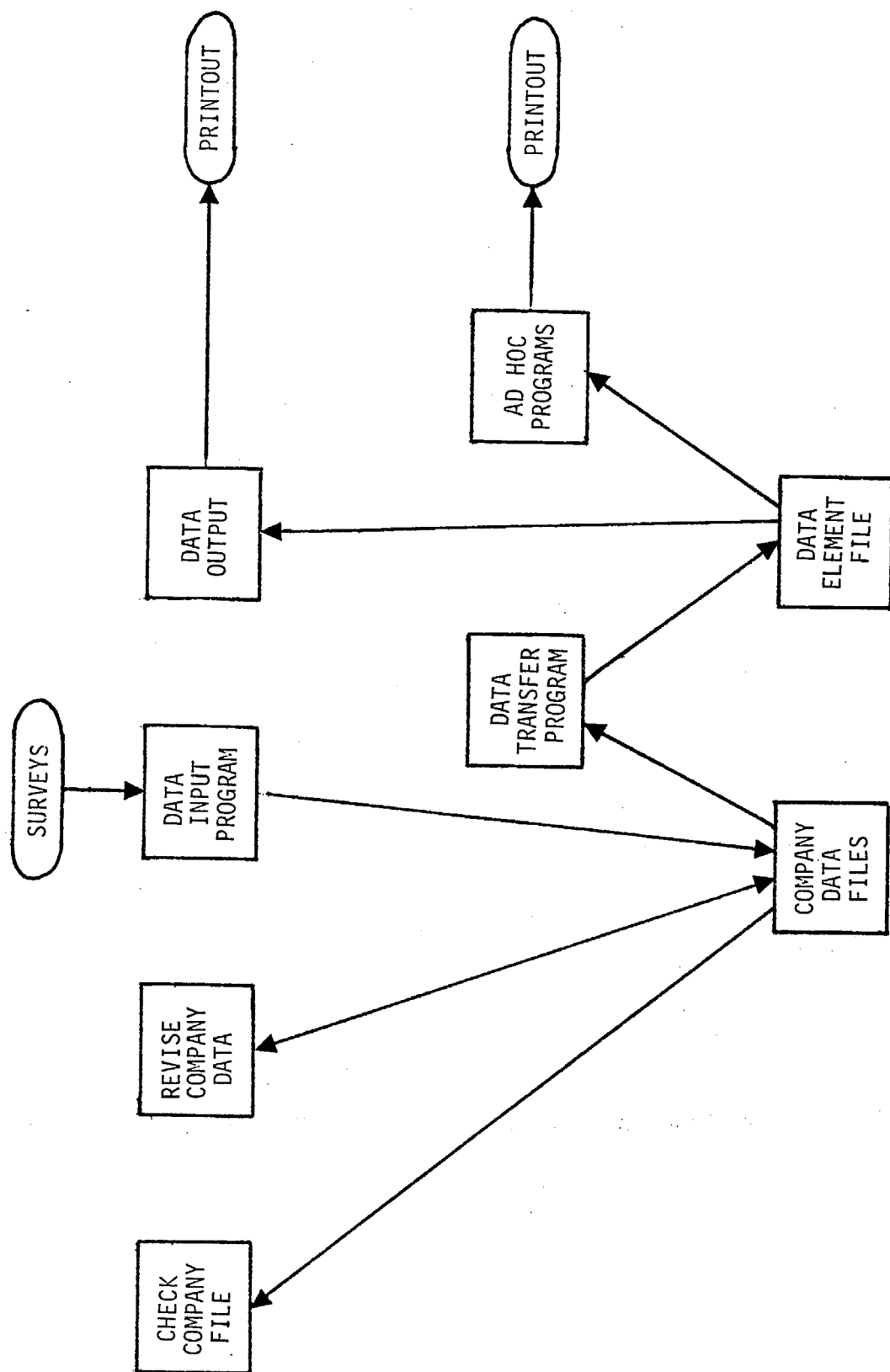


Figure 4.2-1. Data Base Management System

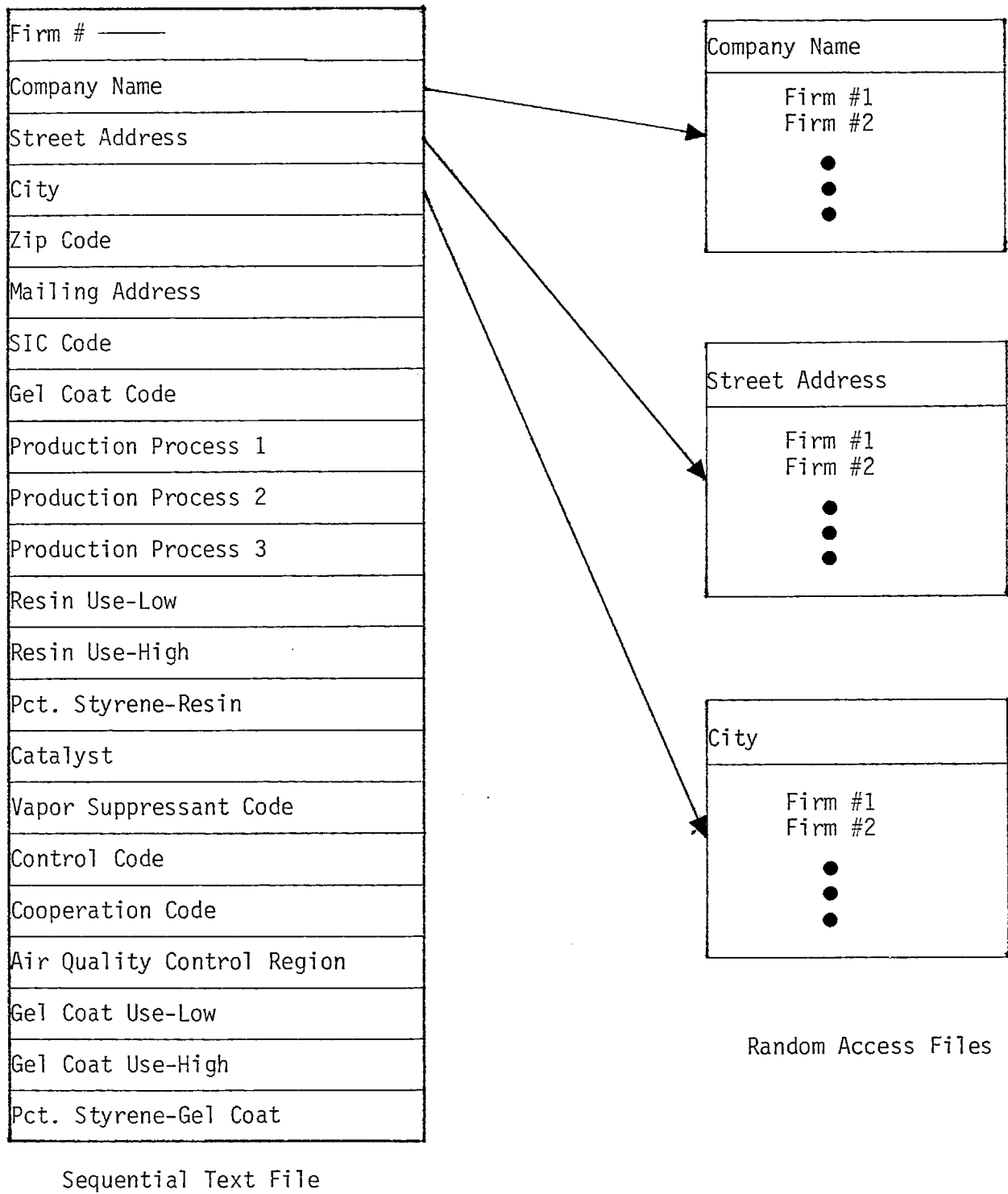


Figure 4.2-2 Structure of Data Files Used For Polyester Resin Use Inventory

- REVISE COMPANY FILE -- This program is used to update a file on a particular company. The user specifies the name of firm, whereupon the program truncates the name to 15 characters and then searches for the corresponding file and stores it in random access memory. The user is then asked to specify the data element to be changed and is shown the value of the element currently stored. After all desired corrections are made, the program erases the old data file and replaces it with the updated version.
- CHECK COMPANY FILE -- If one wishes only to see what data are in a particular company file, then this program is used. The user specifies the company name, which the program truncates to 15 characters and uses to search the disk. When the appropriate file is found, all the data elements contained therein are displayed.
- DATA ITEM TRANSFER -- This program is used to transfer a single data element (e.g., resin use rate) from each company file to a data element file. First, the data element is retrieved from each company file and stored in random access memory. The type of file to be created is called a "random access file," since any of its records may be retrieved immediately by means of a record number. In this case, each company in the inventory is given a unique record number. Because the length of each record in a random access file must be identical, the program sets the record length equal to one plus the size of the largest data element retrieved. For example, the longest company name has 40 characters, so all the records in the COMPANY NAME file are 41 characters long. After all of the individual company files have been searched, the data are transferred from the random access memory onto the disk.
- DATA OUTPUT -- The function of this program is to translate the coded data in the company files to a conveniently read form. It was used to generate the emission inventory summaries provided under separate cover to the ARB.

4.3 CHARACTERISTICS OF THE INDUSTRY IN CALIFORNIA

4.3.1 Survey Response

Using the information sources described in Section 4.1, we identified and attempted to contact 947 putative unsaturated polyester resin users. Table 4.3-1 summarizes the status of our survey as of 15 May 1981, after which date no further attempts were made to obtain new information. In the table, "unsuccessful contacts" are those firms which were either obviously not polyester resin users (for example, those which had gone out of business) or whose user status could not be determined. Only 15 firms out of the 947 refused totally to cooperate with the survey.

It may be seen in Table 4.3-1 that about 15 percent of the firms in the survey had gone out of business or had moved out of California. This result was but one of several symptoms of the depressed state of the industry during the survey period (August 1980 to May 1981). Quite a few companies told our interviewers that they were operating fewer days per week than usual, and/or using less than the normal amount of resin and gel coat. As was described in Section 3.2.3, the marine industry was especially affected.

"Successful contacts" include firms which completed and returned questionnaires, or which were interviewed on the telephone by SAI staff. Also included are three companies for which we received information from local air pollution control districts.

In the following discussion, it is necessary to distinguish between two survey data sets. The first includes complete information on 291 firms, and was used to calculate various industry characteristics, such as median firm size; it is called the "statistical data set." The other, which is displayed in Table 4.3-2, includes the partial data obtained for an additional 14 firms, and is called the "supplementary data set." Wherever possible, we have combined information from the two. An inventory of all 305 firms has been supplied to the ARB as a separate document.

4.3.2 Statewide Unsaturated Polyester Resin Use

A major "unknown" at the start of this study was the size of the polyester resin/fiberglass industry in California. Discussions with a major resin formulator in July 1980 led to an initial estimate of 59 to 63 million

Table 4.3-1
POLYESTER RESIN/FIBERGLASS SURVEY STATUS

<u>Total Plants in Survey</u>	<u>947</u>
-------------------------------	------------

<u>Unsuccessful Contacts</u>	<u>229</u>
------------------------------	------------

- | | |
|---|-----|
| - Out of Business/Moved from California | 139 |
| - Not a Manufacturing Plant | 64 |
| - Refused to Cooperate | 15 |
| - Duplicate Plant | 7 |
| - Unable to Reach | 4 |

<u>Successful Contacts</u>	<u>718</u>
----------------------------	------------

- | | |
|---------------------------|-----|
| - Telephone Interviews | 635 |
| - Written Questionnaires | 80 |
| - Information from APCD's | 3 |

<u>Polyester Resin Users</u>	<u>305</u>
------------------------------	------------

- | | |
|---------------------------------|-----|
| - Complete Information Obtained | 291 |
| - Partial Information Obtained | 14 |

Table 4.3-2
SUPPLEMENTARY DATA SET

Survey I.D. No.	County	Product	Processes	Total Resin Use (lb/yr)	VS	Control Code
40	Santa Clara	Auto parts	Hand, Spray	ND	Yes	6
77	Santa Clara	ND ^a	Spray	ND	ND	ND
151	San Diego	Boats	ND	ND	ND	ND
177	Los Angeles	Panels	ND	26,000	No	6
190	Los Angeles	Boats	Hand	ND	No	ND
227	Orange	ND	ND	ND	ND	ND
577	Los Angeles	General	Bag molding	ND	ND	ND
643	San Diego	Marble	Casting	ND	ND	ND
654	Los Angeles	Spas	Spray	312,000	No	6
669	Orange	Rods	Pultrusion	ND	ND	ND
688	Los Angeles	Boats	ND	ND	ND	ND
810	Orange	ND	Hand	ND	ND	8
832	Marin	ND	ND	ND	ND	ND
901	Alameda	Spas	ND	ND	ND	ND

^aND = No data

kg/yr (130 to 140 million lb/yr) total polyester resin consumption in the State. The full impact of the recession in the boat building industry had not yet been felt, however, and in January 1981 the same source told us that 45 million kg/yr (100 million lb/yr) would be more likely. In both cases, one estimate was made by multiplying national resin use by a "rule-of-thumb" factor. Attempts were made to obtain another estimate. The Society of the Plastics Industry, Inc.'s Committee on Resin Statistics, which compiles nationwide use data for a wide variety of resins and plastic products, does not have data for individual states (Anon., 1981a), nor does the Readers Service of Modern Plastics (Anon., 1981b).

We feel reasonably confident, therefore, that our estimate of 44.4 to 45.5 million kg/yr (97.9 to 100.4 million lb/yr) for California unsaturated polyester resin use is the best available to the general public. Although many very small firms might have remained unidentified, their combined resin use would constitute but a tiny fraction of the statewide total. Furthermore, after discussions with cognizant air pollution control agencies, we believe that no major user has escaped our detection.

4.3.3 Distribution of Resin Users by Size and Location

Distribution by Size

It is clear from our survey data that the California polyester resin/fiberglass industry consists of a relatively large number of small firms which, in combination, account for only a small fraction of the state's unsaturated polyester resin consumption; and a few very large firms, which use the great majority of the total resin. Figure 4.3-1 shows the cumulative frequency distribution of fabricators by firm size, which is defined here as total resin use (laminating and casting resin, plus gel coat) per firm. A logarithmic scale was necessary for firm size, since this variable ranged from 99.77 kg/yr to 8.76 million kg/yr (220 lb/yr to 19.3 million lb/yr). As seen in the figure, the median firm size is about 27,500 kg/yr (60,200 lb/yr). More than 168 companies use less than 45,000 kg/yr (100,000 lb/yr).

Figure 4.3-2 gives another picture of the way that large companies dominate resin consumption in California. The graph is an analogue of the Lorenz curve in economics, which is used to measure the distribution of market share or income among firms (Asch, 1970). The diagonal line represents a

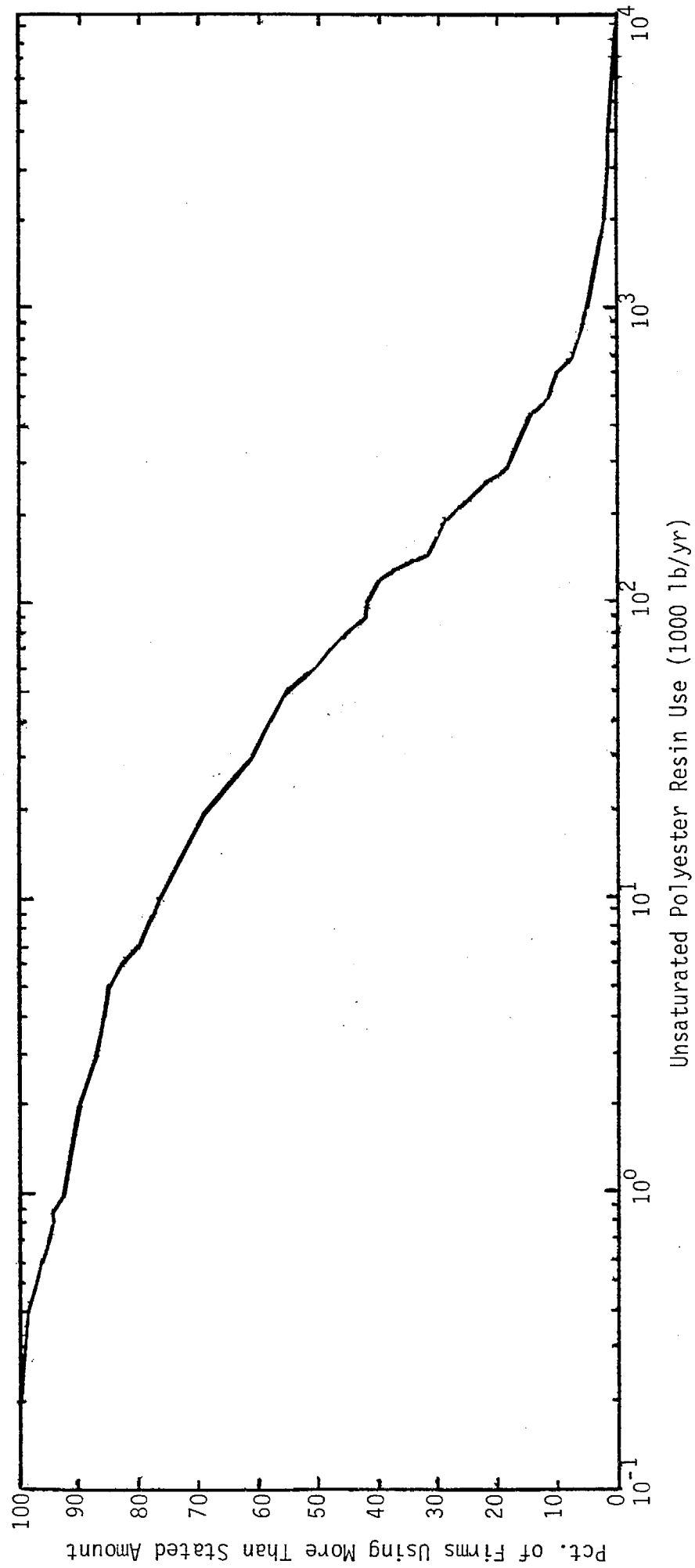


Figure 4.3-1. Cumulative Frequency Distribution of Polyester Resin/Fiberglass Fabricators, by Resin Use

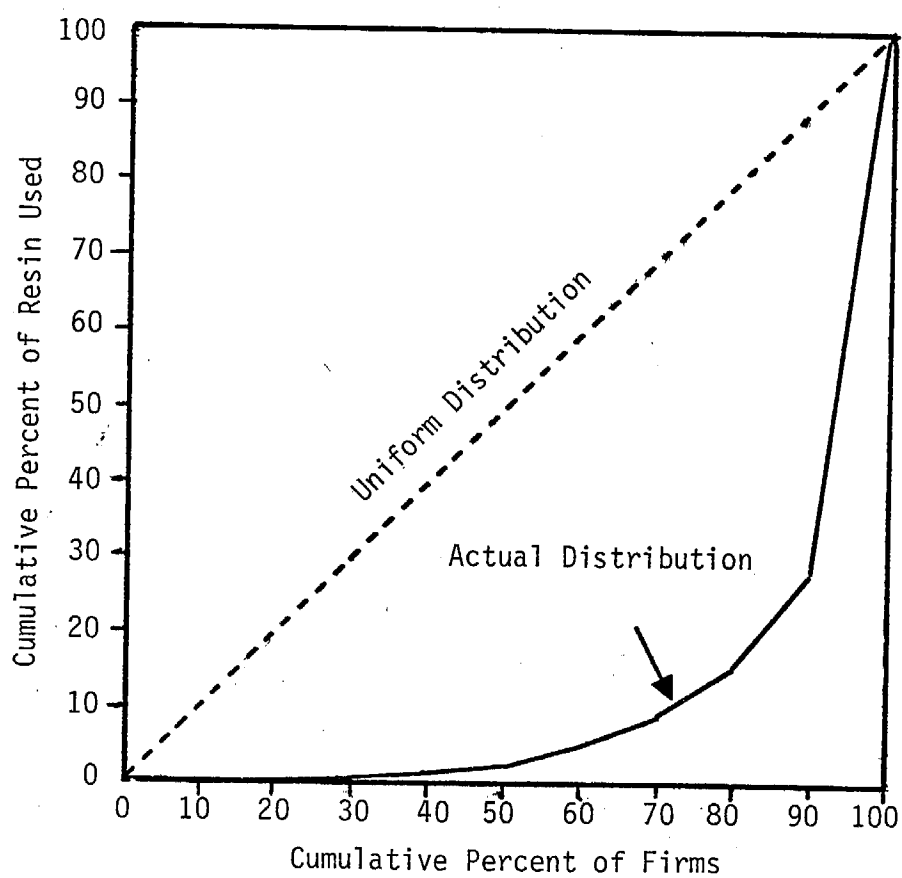


Figure 4.3-2. Lorenz Curve for Distribution of Polyester Resin Use in California

condition in which all firms use the same amount of resin. The Gini coefficient, defined as the ratio of the area between the two curves to the area under the diagonal, theoretically varies from 0 (uniform market share) to 1 (monopoly). Since this ratio is in our case 0.774, the use of polyester resin is indeed highly concentrated. For example, the largest 10 percent of the firms consume 72 percent of the resin. As will be discussed in Chapter 10, a major implication of this finding is that it may be cost-effective to focus attention upon control of emissions from this relatively small subpopulation of the industry.

Distribution by County

At least one polyester resin/fiberglass fabricator was identified in 32 of California's 58 counties. Counties where no polyester resin users were identified are listed in Table 4.3-3. It is entirely possible that one or two--or even several--small operations exist in these areas, but emissions from those firms would likely be negligible. Table 4.3-4 gives our survey results for the remaining counties. Information from the supplementary data set has been included where possible. Note that both a lower and an upper estimate are given for total resin use (laminating and/or casting resin plus gel coat). In many cases, survey respondents gave upper and lower estimates for their resin use (e.g. "five to ten drums per week"); these bounds were carried through the entire data analysis. Note also that, to assure the confidentiality of data from individual users, resin use is not reported here for counties having fewer than three firms. The unidentified resin use in the Table is about 2.1 to 2.4 million kg/yr (4.5 to 5.2 million lb/yr), or about 5 percent of the statewide use.

The polyester resin/fiberglass industry in California is evidently centered in Los Angeles, Orange and San Diego Counties, which in combination account for 193 firms (63 percent of the total) and about 81 percent of the polyester resin consumption in the state. The next largest resin-using counties are Santa Clara, Sacramento, and Alameda, whose 43 firms account for another 4 percent of the state's resin use. Most of the large firms are in Southern California, although the average resin use per firm in Sacramento, San Joaquin and Yolo Counties is actually higher than in Los Angeles and Orange Counties.

Table 4.3-3
COUNTIES WITH NO REPORTED POLYESTER RESIN USE

Alpine	Mariposa
Amador	Mendocino
Butte	Modoc
Calaveras	Mono
Colusa	Monterey
Del Norte	Nevada
El Dorado	Plumas
Humboldt	Riverside
Imperial	Sierra
Inyo	Siskiyou
Kings	Stanislaus
Lake	Trinity
Lassen	Tuolumne

Table 4.3-4
REPORTED POLYESTER RESIN USE, BY COUNTY

County	No. of Firms ^a	Reported Polyester Resin Use	
		Lower Estimate (lb/yr)	Upper Estimate (lb/yr)
Alameda	11	817,800	1,018,900
Contra Costa	7	812,400	818,000
Fresno	8	323,580	323,580
Glenn	1	x ^b	x
Kern	2	x	x
Los Angeles	76	31,243,400	31,593,200
Madera	1	x	x
Marin	5	74,600	74,600
Merced	1	x	x
Napa	1	x	x
Orange	74	40,638,600	41,474,600
Placer	1	x	x
Sacramento	12	710,600	993,200
San Benito	1	x	x
San Bernardino	3	1,936,700	1,936,700
San Diego	43	8,549,600	8,587,700
San Francisco	4	120,900	149,400
San Joaquin	3	1,561,400	1,626,400
San Luis Obispo	1	x	x
San Mateo	5	822,200	822,200
Santa Barbara	1	x	x

(continued on next page)

Table 4.3-4
REPORTED POLYESTER RESIN USE, BY COUNTY
(continued)

County	No. of Firms ^a	Reported Polyester Resin Use	
		Lower Estimate (lb/yr)	Upper Estimate (lb/yr)
Santa Clara	20	2,091,100	2,091,100
Santa Cruz	2	x	x
Shasta	6	998,300	998,300
Solano	1	x	x
Sonoma	2	x	x
Sutter	1	x	x
Tehama	1	x	x
Tulare	4	393,800	426,300
Ventura	3	244,800	257,900
Yolo	3	1,987,800	1,987,800
Yuba	1	x	x
Totals	305	97,888,000	100,414,200

^a Includes 12 firms for which resin use data are lacking.

^b To preserve the anonymity of individual firms, county totals are presented only for counties have three or more users.

Distribution by Air Quality Control Region

To aid in coordination with statewide emission inventory data, our results were also grouped according to Air Quality Control Region (AQCR), as defined by the U.S. Environmental Protection Agency. (See Figure 4.3-3). AQCR boundaries correspond fairly well to those of the California Air Basins, which are shown in Figure 4.3-4; the chief exception is that Ventura County is included in AQCR 24 rather than 32. It should be noted that San Bernardino and Riverside Counties are divided between AQCR's 24 and 33; however, the polyester resin/fiberglass fabricators identified by our survey in these counties all are within AQCR 24, which corresponds to the South Coast Air Basin.

Table 4.3-5 shows number of firms and reported polyester resin use for each California AQCR having at least one firm. It is clear that the great majority of the firms and the resin use are centered in AQCR 24. The San Diego Air Basin (AQCR 29) is a distant second in resin use, while the San Francisco Bay Area (AQCR 30) and the Sacramento Valley (AQCR 28) Air Basins are tied for third.

4.3.4 Products and Production Processes

Products

As mentioned in Section 4.2.1, SIC codes are inadequate to identify unsaturated polyester resin users. We therefore defined the set of finished product classifications shown in Table 4.2-4 and asked each firm in our survey to specify the type(s) of products it produced. In many of the cases in which firms did not answer this question, we were able to obtain the information from the California Manufacturers Register. The results are reported in Table 4.3-6.

It was noted above that polyester resin use in California is concentrated among a small number of firms; the same holds true for product categories. The 16 firms which manufacture panels and bathroom fixtures use almost 25 million kg/yr (55 million lb/yr) of resin and gel coat, or about 55 percent of the state total. The greatest number of firms are in the boat building, synthetic marble and general job shop categories. While comprising over half of the user population, however, they account for only about one quarter of the total unsaturated polyester resin use.

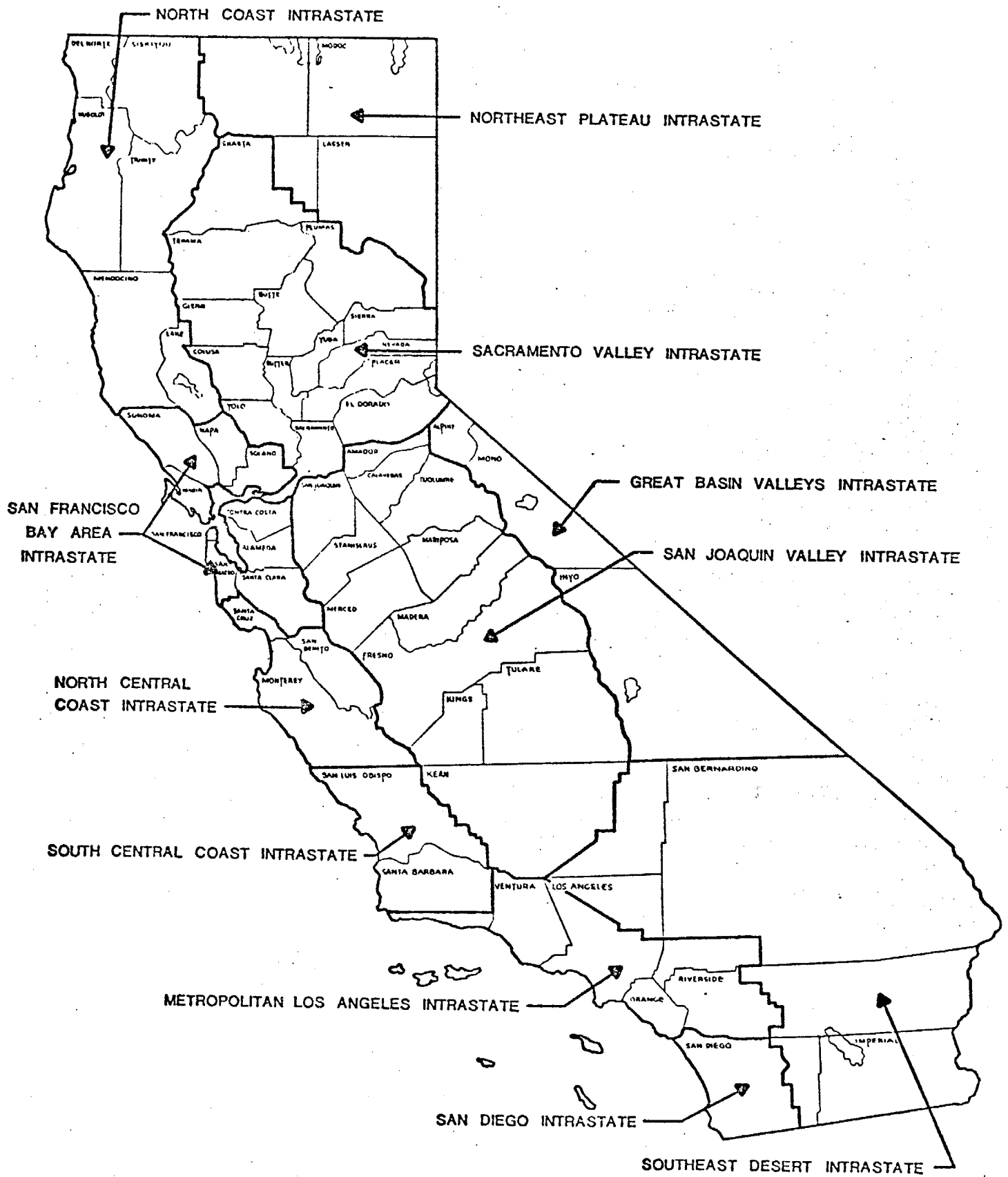


Figure 4.3-3. Federal Air Quality Control Regions in California.

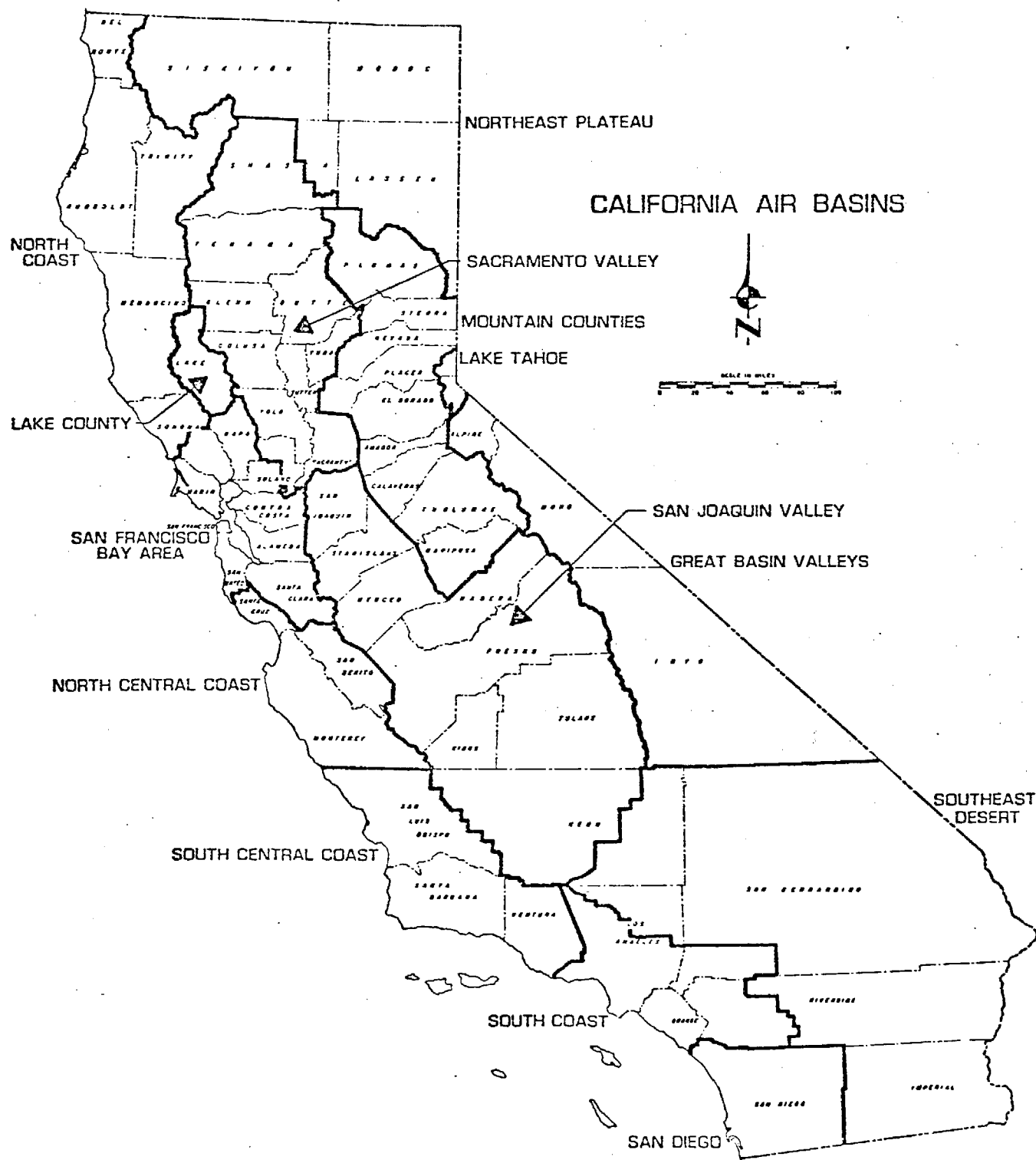


Figure 4.3-4. California Air Basins

Table 4.3-5

REPORTED POLYESTER RESIN USE, BY AIR QUALITY CONTROL REGION

AQCR No.	California Air Basin Name	No. of Firms	Estimated Resin Use ^a Lower (lb/yr)	Estimated Resin Use ^a Upper (lb/yr)	Percent of State Total Resin Use ^b
24	South Coast ^c	156 ^d	74,063,500 ^c	75,262,400 ^c	74.95
25	North Central Coast	3	774,400	1,424,400	1.42
28	Sacramento Valley	26	5,203,500	5,489,200	5.47
29	San Diego	43 ^d	8,549,600	8,587,700	8.55
30	San Francisco Bay Area	56 ^d	5,262,100	5,497,300	5.47
31	San Joaquin Valley	19	3,441,300	3,551,800	3.54
32	South Central Coast ^e	2	593,600	601,400	0.60
Totals		305	97,887,400	100,414,100	100.00

^aIncludes laminating and casting resin and gel coat.^bBased upon upper use estimate.^cIncludes Ventura County.^dIncludes firms for which only partial data are available.^eExcludes Ventura County.

TABLE 4.3-6

CALIFORNIA UNSATURATED POLYESTER RESIN USE BY PRODUCT TYPE
(Statistical Data Set)

Product	No. of Firms	Polyester Resin Use Lower Estimate	(lb/yr) Upper Estimate	Pct. of Total UP Resin Use in California ^a	Average UP Resin Use Per Plant (lb/yr)
Boat Building, Repair	79	13,474,000	14,085,000	14.1	178,300
Synthetic Marble	50	9,701,000	9,773,000	9.8	195,500
General	25	1,300,000	1,316,000	1.3	52,600
Tanks, Containers	22	4,473,000	5,364,000	5.4	243,800
Auto, Aircraft, Truck	19	1,186,000	1,259,000	1.3	66,300
Spas, Hot Tub	9	1,491,000	1,712,000	1.7	190,300
Surfboards	8	122,000	122,000	0.1	15,200
Panels	8	44,864,000	44,936,000	44.9	5,617,000
Bathroom _b Fixtures	8	9,781,000	9,781,000	9.8	1,222,600
Furniture	7	2,791,000	2,791,000	2.8	398,700
Pipes, Ducts	6	493,000	493,000	0.5	82,200
Electronics	5	903,000	938,000	0.9	187,700
Antennas, Rods	5	1,643,000	1,643,000	1.6	328,600
On-site Repairs	4	138,000	138,000	0.1	34,500
Swimming Pools	3	542,000	542,000	0.5	180,600

(Continued next page)

TABLE 4.3-6
CALIFORNIA UNSATURATED POLYESTER RESIN USE BY PRODUCT TYPE
(Statistical Data Set)
(continued)

Product	No. of Firms	Polyester Resin Use(lb/yr) Lower Estimate	Upper Estimate	Pct. of Total UP Resin Use in California ^a	Average UP Resin Use Per Plant(lb/yr)
Helmets, Sporting Goods	2	269,000	317,000	0.3	158,600
Radomes	1	29,000	29,000	0.1	29,000
Not Reported	30	4,348,000	4,835,000	4.8	161,179
TOTALS	291	97,548,000	100,074,000	100.0	343,900

^aBased upon upper use rate estimate

^bDoes not include fixtures made of synthetic marble

The resin use rate per firm varies significantly from product to product. Panel and bathroom fixture plants are relatively large, averaging 2.5 million kg/yr (5.6 million lb/yr) and 550,000 kg/yr (1.2 million lb/yr) per firm, respectively. The smallest operations are the surfboard manufacturers, who average only 6,900 kg/yr (15,000 lb/yr) per firm. We believe that the number of surfboard firms is probably significantly under-reported, since there are many backyard or garage operations which we could not identify. Because these enterprises are so small, however, their omission most likely has no effect upon estimates of statewide totals.

Production Processes

Table 4.3-7 shows the results of our survey of fabrication processes used in the California polyester resin/fiberglass industry. The table shows reported uses of each process; since many firms use more than one process, the total number of firms and total resin use exceed the values reported in other tables. It is clear that, despite recent increases in use of more sophisticated production processes, the firms surveyed which use hand layup are by far the most common. About one third of the firms surveyed use hand layup only, while almost three quarters of them use either hand or spray layup or a combination of the two.

The average resin consumption per reported use of each process is also shown in Table 4.3-7. It is clear that continuous lamination and pultrusion are high-volume operations, while hand layup processes use relatively little resin per firm. In fact, firms which use only hand and/or spray layup, though many in number, account for only 60 percent of the statewide total consumption.

4.3.5 Cross-Linking Agents and Catalysts

All but three plants reported that they used styrenated resin or did not know the cross-linking agent. Discussions with resin and gel coat formulators lead us to believe that use of monomers other than styrene is quite rare in California. The three exceptions all use resin containing methyl methacrylate (MMA). Since two of these plants are among the largest in the state, the use of these resins accounts for almost 12 percent of the statewide total. The two large firms make fiberglass panels, while the third is a boat manufacturer. A fourth company, also a panel manufacturer, uses a mixture of styrene and methyl methacrylate on occasion.

TABLE 4.3-7
USE OF PRODUCTION PROCESSES BY
CALIFORNIA POLYESTER
RESIN/FIBERGLASS FABRICATORS

Process	No. of Firms	Total Resin Use ^a (lb/yr)	Average Consumption per use of Process ^b (lb/yr)
Hand layup	214	26,827,000	127,140
Spray layup	149	56,741,300	386,500
Marble casting	49	9,248,400	192,670
Filament winding	9	2,972,100	330,240
Bag Molding	9	1,463,900	182,980
Pultrusion	6	5,138,000	856,330
Continuous lamination	4	21,110,000	5,277,500
Matched metal molding	1	737,000	737,000
Other	5	479,620	95,924
Unknown	1	ND ^c	ND
Hand layup only		98	97,243
Spray layup only		41	981,521
Hand and spray layup only		77	132,059

^aBased upon upper estimate of resin and gel coat use.

^bBased upon 291-firm statistical data set

^cND = No data

It should be noted that one major gel coat manufacturer told us that its formulations contain a 60:40 mixture of styrene and MMA. We do not have sufficient data to estimate the share of the total statewide gel coat use represented by this formulation.

As seen in Table 4.3-8, methyl ethyl ketone peroxide (MEKP) is by far the most widely-used catalyst; only eight percent of the firms in the survey use anything else. The second most commonly-used catalyst is benzoyl peroxide (BP). Although this chemical is frequently associated with high-temperature processes, there did not appear to be any clear pattern of use among the firms surveyed, except that firms using BP tend to be rather large. The only other catalyst cited more than once was 2,4-pentanedione peroxide, which is used by two marble manufacturers and one maker of electronic parts.

4.3.6 Emission Control Techniques

Although each firm was asked whether it attempted to remove or reduce organic vapor emissions, the major objective of this part of the survey was to determine the pathways by which the vapors are transferred from the production processes to the outdoor ambient air. Knowledge of these pathways was important both for selection of emission test sites and for estimating the extent of ventilation changes necessary should an exhaust gas treatment strategy be considered. Since treatment processes such as absorption and incineration require channelling of exhaust gases, those plants already having a ducting system would have smaller retrofitting requirements.

Table 4.3-9 shows the result of this portion of our survey. Definitions of the different emission modes were given in Section 4.2.1. About 36 percent of the firms, representing over 62 percent of the state's resin use, already have some form of ducting. Given state and federal limitations on occupational exposure, it is not surprising that only 38 firms, representing less than 5 percent of statewide resin use, use natural ventilation to control indoor exposures. Another 30 firms operate outdoors or make repairs off-site.

Only two firms reported using organic vapor removal equipment. In each case, incineration was the reported method. (Emissions from one of these plants were measured as part of this project; see Section 5.2.1.) Two other plants direct their exhaust through a water spray "curtain," but the purpose of this treatment is to remove particulate matter. One large plant reported that

TABLE 4.3-8
USE OF CATALYSTS BY CALIFORNIA POLYESTER
RESIN/FIBERGLASS FABRICATORS

Catalyst Type	No. of Firms	Pct. of Firms	Total Resin Use ^a (lb/yr)	Pct. of Total Resin Use
MEK peroxide (MEKP)	269	92.44	73,183,100	73.13
Benzoyl peroxide (BP)	6	2.07	9,454,120	9.45
Cumene hydroperoxide	1	0.34	6,500,000	6.49
Cumene peroxide + BP	1	0.34	5,200,000	5.20
BP in resin, MEKP in Gel coat	2	0.69	2,693,600	2.69
2,4-pentanedione peroxide	3	1.03	1,086,580	1.09
Peroxydicarbonate	1	0.34	421,000	0.42
Other	5	1.72	1,054,960	1.05
Do not know	3	1.03	482,900	0.48
TOTALS	291	100.00	100,076,260	100.00

^aBased upon upper estimate of resin and gel coat use.

TABLE 4.3-9

DISTRIBUTION OF VAPOR EMISSION MODES IN THE
CALIFORNIA POLYESTER RESIN/FIBERGLASS INDUSTRY

Emission Mode	No. of Firms	Pct. of Firms	Total Resin Use ^a (lb/yr)	Pct. of Total Resin Use
<u>Outdoor Operation</u>	30	10.31	742,920	0.74
<u>Passive Ventilation</u>				
Wall vents only	18	6.18	1,778,660	1.78
Ceiling vents only	10	3.44	1,673,240	1.67
Wall and ceiling vents	10	3.44	1,201,010	1.20
<u>Forced Air/Vents</u>				
Wall vents only	31	10.65	4,003,450	4.00
Ceiling vents only	43	14.78	9,444,600	9.44
Wall and ceiling vents	23	7.90	5,119,880	5.12
<u>Ducted Pathways</u>				
General work area to wall	4	1.37	2,279,640	2.28
General work area to roof	25	8.59	19,409,180	19.39
General work area to wall and roof	2	0.69	1,445,300	1.44
Spray booths to wall	9	3.09	2,850,380	2.85
Spray booths to roof	66	22.68	36,168,930	36.14

(continued on next page)

TABLE 4.3-9

DISTRIBUTION OF VAPOR EMISSION MODES IN THE
CALIFORNIA POLYESTER RESIN/FIBERGLASS INDUSTRY
(continued)

Emission Mode	No. of Firms	Pct. of Firms	Total Resin Use ^a (lb/yr)	Pct. of Total Resin Use
<u>Special Controls</u>				
Water curtain	2	0.69	267,800	0.27
Afterburner	2	0.69	11,920,000	11.91
<u>Unknown</u>	16	5.50	1,771,260	1.77
TOTALS	291	100.00	100,076,250	100.00

it had been considering purchasing a wet scrubber system, while another is considering substituting foamed polyester for conventional liquid resin. It should be noted that the plants using afterburners are both quite large, use a continuous lamination process, and consume about 12 percent of the industry's unsaturated polyester resin. The combination of high operating temperatures and large potential organic vapor emissions apparently made use of incineration economical.

Firms were also asked to report whether they used resin or gel coat containing vapor suppressant compounds. A total of 54 companies, representing 25 percent of the statewide polyester resin and gel coat use, definitely use vapor-suppressed resins, while 113 firms, representing 40.5 percent of the unsaturated polyester resin use, definitely do not. The most frequent response to our survey was "do not know." All but one of the resin and gel coat formulators we contacted said that they do not add a suppressant to a resin unless the customer specifically asks them to do so. The exception stated that all its resin and gel coat contains a vapor suppressant, unless the customer does not want it. Although identification of resin and gel coat source was not requested in all cases, 22 firms, representing 2.5 percent of statewide resin use, reported that they used the brand in question. It is possible, therefore, that at least 1.25 million kg/yr (2.75 million lb/yr) of resin and gel coat contain a vapor suppressant.

An attempt was made to see whether producers of various products tended to use vapor suppressant. The greatest number of firms using suppressed resins were in the boatbuilding industry. It may be recalled, however, that this product category contains the most firms among polyester resin users in general. Chi square analysis showed that there is no statistically significant association ($p > 0.05$) of vapor suppressant use with product category ($\chi^2 = 19.452$, d.f. = 16).

4.4 REFERENCES

Anon. 1981a. Society of the Plastics Industry, Inc., Committee on Resin Statistics, New York, New York. Personal communication (26 February 1981).

Anon. 1981b. Modern Plastics, Readers Service, New York, New York. Personal communication (26 February 1981).

Asch, P. 1970. Economic theory and the antitrust dilemma. John Wiley and Sons, Inc., New York, pp. 154-155.

TABLE 4.3-10
USE OF VAPOR SUPPRESSANTS BY CALIFORNIA
POLYESTER RESIN/FIBERGLASS FABRICATORS

User Status	No. of Firms	Pct. of Firms	Total Resin Use ^a (lb/yr)	Pct. of Total Resin Use
Yes, in resin and gel coat	17	5.84	4,997,020	4.99
Yes, but not in gel coat	35	12.03	19,374,530	19.36
Yes, no gel coat used	2	0.69	720,000	0.72
No	113	38.83	40,525,730	40.50
User does not know	124	42.61	34,458,960	34.43
TOTALS	291	100.00	100,076,240	100.00

^aBased upon upper estimate of resin and gel coat use.

Burns, L., Air Pollution Inspector, Shasta County Air Pollution Control District, Redding, California. Personal communication (15 August 1980).

California Manufacturers Association. 1980. 1980 California Manufacturers Register, 33rd Edition. Times Mirror Press, Los Angeles.

The Society of the Plastics Industry, Inc. 1980. 1980 membership directory and buyers guide. The Society of the Plastics Industry, Inc., New York.

U.S. Environmental Protection Agency. 1981. AEROS manual of codes, National Air Data Branch, Monitoring and Data Analysis Division, EPA-450/2-76-005 (Update V-4).

5.0

DERIVATION OF EMISSION FACTORS

Air pollution control agencies and the industries they regulate are faced continually with the problem of estimating pollutant emissions in the absence of hard, site-specific scientific data. A very common practice is to assume that emissions are a fixed fraction of the material consumed, processed, produced, stored or disposed of by a facility. These fractions, whose scientific bases range from "engineering judgment" to comprehensive field and laboratory studies, are called emission factors. In the case of the polyester resin/fiberglass industry, emission factors are generally expressed as mass of volatile organic compound (VOC) emitted per unit mass of polyester resin consumed in the manufacturing process. For example, the South Coast Air Quality Management District instructs its permit holders to compute their annual emission fees under the assumption that VOC emissions are five and ten percent of laminating resin and gel coat consumption, respectively (MacKnight 1981).

After reviewing the literature, performing laboratory and source emission tests, and discussing the matter with polyester resin users, we believe that using a single emission factor for all cases can lead to serious inaccuracies in predicting VOC emissions. First, as was discussed in Section 3.3, polyester resin/fiberglass processes vary considerably in their emission potential. Second, resins have a wide range of volatile monomer content, so that emission factors based only upon resin mass would often be incorrect. Third, the use of vapor suppressants is frequently not accounted for. Finally, the microenvironment of a production process (temperature, wind speed etc.) can strongly influence evaporation rates. A more realistic approach to defining and applying emission factors would take these realities into account. We have therefore chosen to develop emission factors for each of the major production processes, and to base them upon the input of monomer, rather than resin. These emission factors are defined as:

$$\text{Emission Factor} = \frac{(\text{Mass VOC emitted})}{(\text{Mass VOC input})}$$

Another way of stating this is:

$$\text{Emission Factor} = \frac{(\text{Mass VOC emitted})}{(\text{Mass resin consumed}) \times (\text{Fraction monomer in resin})}$$

The next three sections are devoted to our literature review, emissions tests, and laboratory tests. Process-specific emission factors are then derived in Section 5.4.

5.1 REVIEW OF PREVIOUS ESTIMATES

Several attempts have been made to measure the emission of volatile organic gases from the application of polyester resin. Table 5.1-1 summarizes the findings of previous tests identified by this project. These results should be interpreted with great care. Experimental conditions, resin types, test procedures, collection methods, and analytical techniques were different in each case. Important data, such as the styrene content of the resin used, were often missing. We have therefore included, for each emission factor estimate, a rating based upon the relative use of experimental data and assumptions. Table 5.1-2 shows the rating system.

5.1.1 Dade County, Florida Study

One of the earliest attempts to gain an understanding of the nature and quantity of styrene emissions from the polyester resin/fiberglass industry was a study performed by the predecessor of the Metropolitan Dade County Department of Environmental Resources Management in Miami, Florida (Schmitz, 1968). Polyester resin use in Dade County was at that time roughly the same as in Southern California today, and the agency was receiving "frequent complaints" about organic vapor odors around boatbuilding plants and other polyester resin/fiberglass fabrication facilities. In one set of tests, three-ply resin/glass laminates were made by hand layup in a laboratory. A statement that the "resin contained wax" is assumed to imply that a vapor suppressant was present. The author gives the brand name of the resin, but not the styrene percent; our calculations are based upon the knowledge, from our industry survey, that this particular brand of resin contains from 40 to 44 percent styrene. Another set of tests were made at a fabrication plant. The data for only one test, that of a gel coat spray gun, were considered complete enough to use here. Because the Dade County study was done 13 years

EMISSION FACTORS ESTIMATED FROM PREVIOUS STYRENE MEASUREMENT STUDIES

Process	Resin Type ^a	Location	Calculated Emissions Factor (pct) ^b	Rating of Test ^c	Reference ^d
Hand layup	Laminating	Laboratory	8.5 - 10.5	18	1,4
Hand layup	Laminating	Laboratory	15.6 - 35.4	18	5
Hand layup	Laminating*	Laboratory	- 8	16	2
Hand layup	Laminating*	Laboratory	5.6 - 6.3	16	6
Hand layup	Laminating*	Laboratory	1.9 - 2.6	18	4
Hand layup	Laminating*	Laboratory	13.6 - 19.6	18	5
Hand layup	Gel coat	Laboratory	47	16	2
Hand layup	Filament winding	Laboratory	71 - 82	18	4
Hand layup	Filament* winding	Laboratory	16	18	4
Hand layup	(Fire retardant)	Laboratory	6.6	14	2
Hand layup	Casting*	Laboratory	3.8 - 4.1	18	4
Hand layup	Casting	Laboratory	1.0 - 1.4	18	4
Spraygun	Laminating	Field	8 - 18	18	3
Spraygun	Laminating	Field	16 - 25	14	3
Spraygun	Laminating	Field	13	16	3

5.1-1

EMISSION FACTORS ESTIMATED FROM PREVIOUS STYRENE MEASUREMENT STUDIES
(continued)

Process	Resin Type ^a	Location	Calculated Emission Factor (pct) ^b	Rating of Test ^c	Reference ^d
Spraygun	Gel coat	Field	26 - 28	14	3
Spraygun	Gel coat	Field	7 ^e - 12 ^e	16	3
Spraygun	Gel coat	Field	24 - 38	16	3
Chopper gun	Laminating	Field	27	16	3
Chopper gun	Laminating	Field	>12 ^f	10	3

^a Asterisks indicate use of vapor suppressant^b Emission factor = 100 x (styrene emission/styrene input)^c Rating system is explained in Table 5.1-2.^d 1=Ashland Chemical Company (undated); 2=Berryman (1978); 3=DeBoisblanc (1980); 4=Duffy (undated); 5=Pritchard and Swampillai (1978); 6=Schmitz (1968).^e These emission factors are for laminating resin and gel coat combined.^f Since exhaust air was diluted to an unknown extent, this figure is a lower bound on the estimate.

TABLE 5.1-2
SYSTEM FOR RATING EMISSION FACTOR TEST DATA

	<u>Rating</u>
<u>Styrene Emissions</u>	
Direct measurement	5
Assumed to be percentage of total organic vapor	1
<u>Styrene Content of Resin</u>	
Direct assay	5
Manufacturer's data	3
Typical for industry	1
<u>Measurement Site</u>	
Workplace/continuous operation	5
Workplace/intermittent	3
Laboratory	3
<u>Resin Use Rate</u>	
Direct measurement	5
Typical batch	3
Estimate from other data	1

ago, it is likely that the spray guns used were significantly less efficient than those used today.

5.1.2 Bay Area Air Quality Management District Tests

During our visit to the offices of the Bay Area Air Quality Management District (BAAQMD), we were permitted to review reports on emissions tests made at six polyester resin/fiberglass fabrication facilities between 1974 and 1978. When interpreting results, one should bear in mind that the purpose of these tests was to verify compliance with hourly and daily emission standards, not to develop emission factors. The following brief descriptions tell how BAAQMD data were used for our purpose.

BAAQMD Source Test 74146. These tests were made on the exhaust of a booth where gel coat is sprayed onto shower and bathtub molds. In their report, BAAQMD personnel noted that the spray booth intake air was heavily contaminated with styrene from laminating resin spraying. We therefore used the data to estimate an overall emission factor for gel coat and laminating resin. Since the styrene content of the materials was not reported, we assume 38 to 42 percent for the gel coat and 40 to 45 percent for the laminating resin.

BAAQMD Source Test 74192. The test site was a pipe manufacturing plant which has since gone out of business. Measurements were taken during chopper gun application of laminating resin and glass to a rotating mandrel. It is not apparent from the report whether the operation was enclosed, or whether emissions were directed through ducts. Emissions were reported as a percentage of the resin used; to convert these to emission factors, we assumed that the resin contained between 40 and 45 percent styrene.

BAAQMD Source Test 74200. This plant manufactures shower, tub and sink fixtures. Gel coat is applied in a separate spray booth. Since the styrene content of the gel coat was not reported, we assumed 38 to 42 percent. For chopper gun spraying of laminating resin, we assumed that the styrene percentage in 1974 was the same as reported by this company in our survey. The test engineers reported that the exhaust from the chopper gun operations was diluted with an unknown amount of fresh air. Our calculated emission factors are therefore probably too low.

BAAQMD Source Tests 75028 and 75029. At this plant, which manufactures a variety of fiberglass products, gel coat and chopper gun operations are performed at separate stations, each of which is equipped with exhaust fans and ducts to the roof. Gel coat styrene was assumed to be 38 to 42 percent, while laminating resin styrene was reported by the company to be 40 percent.

BAAQMD Source Test 75101. Details on test procedures were unavailable for this case. Emissions were reported for a chopper gun spray booth. For the percentage of styrene in the resin, we used the figure reported by this company in our industry survey (45 percent).

BAAQMD Source Test 76061. At this plant, which manufactures fiberglass containers, resin is applied in three spray booths, each equipped with an exhaust fan and stack. The styrene content of the resin was determined by a special laboratory analysis to be 53.3 percent. On the first test day, three measurements were made on one stack. On the second day, one sample was taken from the same stack, and two were taken from a second stack; the third stack was not tested. The low and high styrene emission rates per stack were 1.8 and 4.2 lb/hr, respectively. For three stacks, then, emissions would be between 5.4 and 12.6 lb/hr. In this case, resin use was reported in gallons per day. To convert to weight, we assumed that the resin had a specific gravity of 1.2.

5.1.3 Ashland Chemical Company Tests

In order to test the effectiveness of vapor suppressants in reducing styrene emissions, Ashland Chemical Company of Columbus, Ohio conducted several tests of weight loss from various resin and resin/glass formulations. In the laminating resin tests summarized in Table 5.1-1, 1-ft², 3-ply laminates were made with a "standard spray-up" resin having a 20-minute gel time. The rate of weight loss is highest up to and slightly beyond the gel time. The emission factors presented in Table 5.1-1 are based upon the weight loss after one hour.

In another test, an isophthalic polyester resin normally used in filament winding and having a nine-minute gel time was formed into 10- and 20-mil films and allowed to cure. Emission factors presented in the table are based upon weight losses after 24 hours. Note that the test does not simulate

filament winding operations. Finally, a composite consisting of 23.5 percent polyester, 26.5 percent styrene, and 50 percent alumina trihydrate (ATH) by weight was tested. Our emission factors are based upon a 30-minute cure time. This last formulation is similar to that used in manufacture of artificial marble.

As with the other experiments reported here, these data should be interpreted with care. Information on experimental conditions is inadequate to permit repetition, and the extent to which they simulate actual operations is unknown.

5.1.4 Shasta County Studies

In 1978, Shasta County performed laboratory tests of gel coat and resin types used at one of the plants within its jurisdiction (Berryman, 1978). One-foot-square glass plates were coated with wax. A gel coat layer was then applied, and the weight loss due to volatile organic emissions was measured over 66 minutes. Glass roving and laminating resin were then added and weight loss was observed for 50 minutes. Finally, weight loss measurements were made after application of a layer of roving and fire-retardant resin. For our estimates of the emission factor, we have used the styrene percentages reported to us by the company in question during our industrial survey.

5.1.5 Kingston Polytechnic Studies

To our knowledge, the only systematic styrene evaporation study published in the peer-review literature was that performed at Kingston Polytechnic's School of Chemical and Physical Sciences in Kingston-on-Thames, England (Pritchard and Swampillai, 1978). Four types of isophthalic polyester resin, with and without a paraffin wax-based vapor suppressant, were used with woven roving or chopped strand glass mat to make laminates. All test laminates were made by hand layup. Styrene losses were determined gravimetrically. In order to determine the effect of various process variables upon styrene emission rates, Pritchard and Swampillai controlled the ambient temperature, air velocity, amount of hand rolling, glass reinforcement type, styrene concentration, and wax concentration.

In general, styrene evaporation increased with increasing wind speed and increasing ambient air temperature. Use of woven roving resulted in

higher emissions than when chopped strand mat was used. One interesting finding was that increasing the hand-rolling time from 10 to 15 minutes resulted in significantly higher styrene losses, for both vapor-suppressed and non-suppressed resins. Because experimental conditions varied from test to test, we calculated ranges of emission factors for resins with and without vapor suppressant.

5.2 SAI SOURCE TESTS

As none of the abovementioned studies included direct measurement of styrene from modern fabrication processes, SAI conducted a field sampling program at three polyester resin/fiberglass fabrication facilities. To identify appropriate facilities to test, we first searched our emission inventory survey file for those plants whose exhaust air was channeled through definable outlets; i.e. those which vented styrene-laden air chiefly through open windows and/or doorways were not considered. Explanatory letters were sent to the manager of each potential testing site, who was then contacted by telephone about a week later. Once the first two facilities were enlisted in the testing program, another selection criterion was added. Because of the interest in determining the effect of vapor suppressants upon styrene emissions, we required that the third facility use a vapor-suppressed resin. Field sampling protocols are included in each of the three field test descriptions. Instrument calibration and analytical procedures are reported in Appendix B.

5.2.1 Source Tests at Facility A

Facility A is a large continuous lamination plant in Los Angeles County. A preliminary site visit was made on 5 March 1981. Emissions measurements were made on the morning and afternoon of 18 March 1981 and on the morning of 19 March 1981. The first day began sunny with no wind and gradually turned cool and overcast. The second morning was cold and overcast, with a moderate wind from the south; rain began as we took our last three samples.

Facility Description

The facility consists of two independent units: the fiberglass panel plant, which was of interest to this study, and a polyvinyl chloride molding plant, which was not. Panels are made on a production line running almost the entire length of the west side of the facility. The following description is

based upon information supplied by the company, as well as our personal observations. Proprietary process information has been omitted.

During our tests, two types of orthophthalic polyester resin were used. The first, which is used to make general purpose panels, contained 35 percent styrene by weight and no methyl methacrylate (MMA). The second, which is used to improve weather resistance, contained 35 percent styrene and 5 percent MMA. Resins and other chemicals are stored in a yard on the north side of the facility. Blending of resin, colorants, catalyst and fillers (calcium carbonate and ATH) occurs in an open vat inside the plant. After the resin batch is thoroughly mixed, it is pumped to the impregnation table.

The impregnation table consists of a heated metal bed over which a cellophane film is passed at a steady rate. The resin is pumped onto the cellophane and spread evenly over the surface by a "doctor blade." Above the conveyor is a chopper which reduces glass roving to short-length fibers. The fibers are deposited gently and evenly over the moving resin-coated cellophane and then forced into the resin by a special squeeze roll. The wetted glass mat is then transported to the end of the impregnation table, where a top layer of cellophane or polyester film is added. A squeeze roll sets the final thickness of the "sandwich" of film, resin, and glass fibers, and seals the edges. The table temperature is about 57°C (135°F) and the belt speed is 0.06 - 0.21 m/s (12 - 42 ft/min). Since the open area is about 6.1 m (20 ft) long, any portion of the resin-glass mixture is exposed to the air for about 28 to 100 seconds.

Curing takes place in a thermostatically-controlled, gas-fired oven. Wooden "shoes" placed transverse to the direction of travel mold the sheet into the desired cross-sectional pattern. The curing time varies with resin type, desired product properties, and production schedule. Oven temperatures are roughly 104°C in the gel zone (Zone 1), 204°C (400°F) in the cure zone (Zone 2) and 177°C (350°F) in the post cure zone (Zone 4). Zone 3 is a covered area with open sides, located between Zones 2 and 4. After curing, the panels are cut longitudinally and crosswise, sprayed with water, and stripped of the film layers.

Emission Control and Exhaust Points

The assembly line is outfitted with a complex system of hoods, ducts, and fans to minimize the contamination of workplace air with organic vapors and particulate matter. In many cases, ducts from two or more potential emission sources are connected to a header and conveyed to the roof. After reviewing plant plans and touring the assembly line and the roof, we identified the roof-level exhaust points listed in Table 5.2-1. Points 111-37 through 111-40 exhaust air directly from the production line, with no attempt at pollutant removal or dilution. Point 111-41 is in a duct conveying air from the impregnation table to an afterburner, while Point 111-42 is the afterburner exhaust. Point 111-43 is the outlet of an electrostatic precipitator which removes resin and glass particles from air collected from several points in the production line.

The plant has several potential passive emission sources, i.e. those through which air flows principally by convection. Among these are 39 skylights, of which 10 were open on the days of our testing. We observed two elbow vents which are permanently open; one of these was sampled as Point 111-45-1. Finally, the rear door of the plant, near the impregnation table, is usually left open. It is designated as Point 111-45-2 in this study.

Figure 5.2-1 shows the locations of the rooftop sampling points. Point 111-45-2, the rear door, is on the north side of the plant. Although the figure is not to scale, it gives an idea of the relative position of the different pollutant-generating operations along the assembly line, which runs from north to south. Figure 5.2-2 shows the physical configuration of each exhaust vent or duct. Dots indicate the points at which our sampling probe was placed.

Sampling Procedure

We began by using a Foxboro Instruments Model OVA-128 organic vapor analyzer ("OVA") as a "sniffer" at all of the exhaust points listed in Table 5.2-1, to obtain a rough idea of the relative importance of each. Points 111-37 through 111-43 were then sampled in numerical order; seven sample collections constituted one round. The first round was conducted on the morning of 18 March, during which time a resin containing 40 percent styrene and no other monomer was being used on the production line. During the other

Table 5.2-1 :
DISCRETE EXHAUST POINTS AT FACILITY A

Code Number	Contributing Styrene Sources	Exhaust Air Flow m ³ /s (cfm)	Exhaust Air Temp °C (°F)	Observations
111-37	Crosscut saw at end of production line	3.8 (8000)	28-30 (82-86)	No odor
111-38	Curing ovens near end of cure; room air	1.4 (3000)	40-48 (104-118)	
111-39	Curing ovens for early part of cure	0.57 (1200)	76-77 (169-171)	Strong styrene odor
111-40	Glass chopper above impregnation table	2.25 (4770)	26-29 (79-84)	Very strong styrene odor; glass fibers
111-41	Impregnation table (Inlet to afterburner)	0.94 (2000)	29-36 (84-97)	
111-42	Afterburner outlet	1.88 (4000) ^a	540-550 (1004-1022)	
111-43	Various sources (exhaust from particle collection system)	0.57 (1200) ^a	20-30 (68-86)	
111-45-1	Passive duct above impregnation table	Negligible	~25 (77)	Strong styrene odor
111-45-2	Rear door of plant; near impregnation table	Negligible	~25 (77)	Extremely strong styrene odor

^a Includes 0.94 m³/s (2000 cfm) of dilution air.

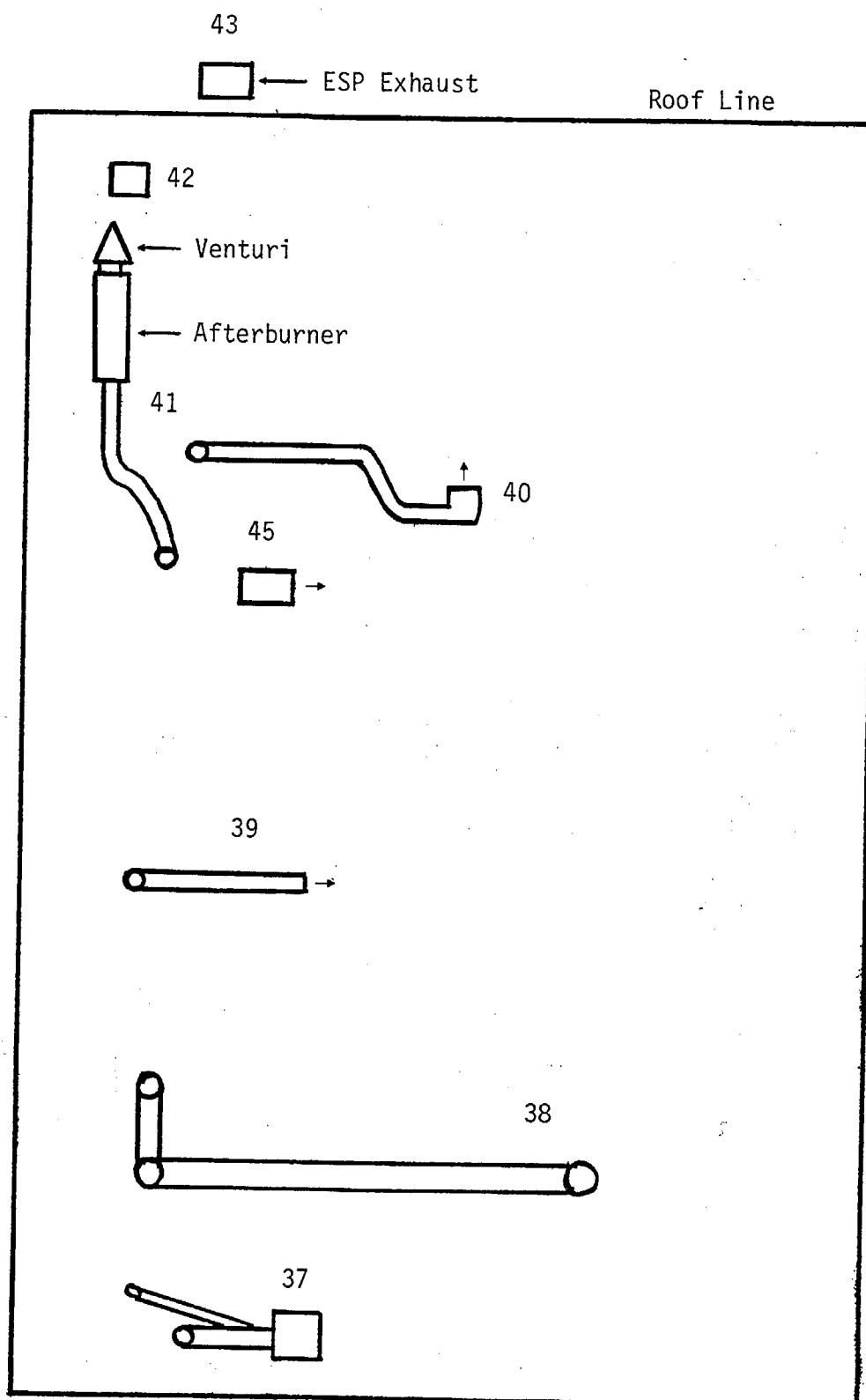


Figure 5.2-1. Locations of Rooftop Sampling Points at Facility A

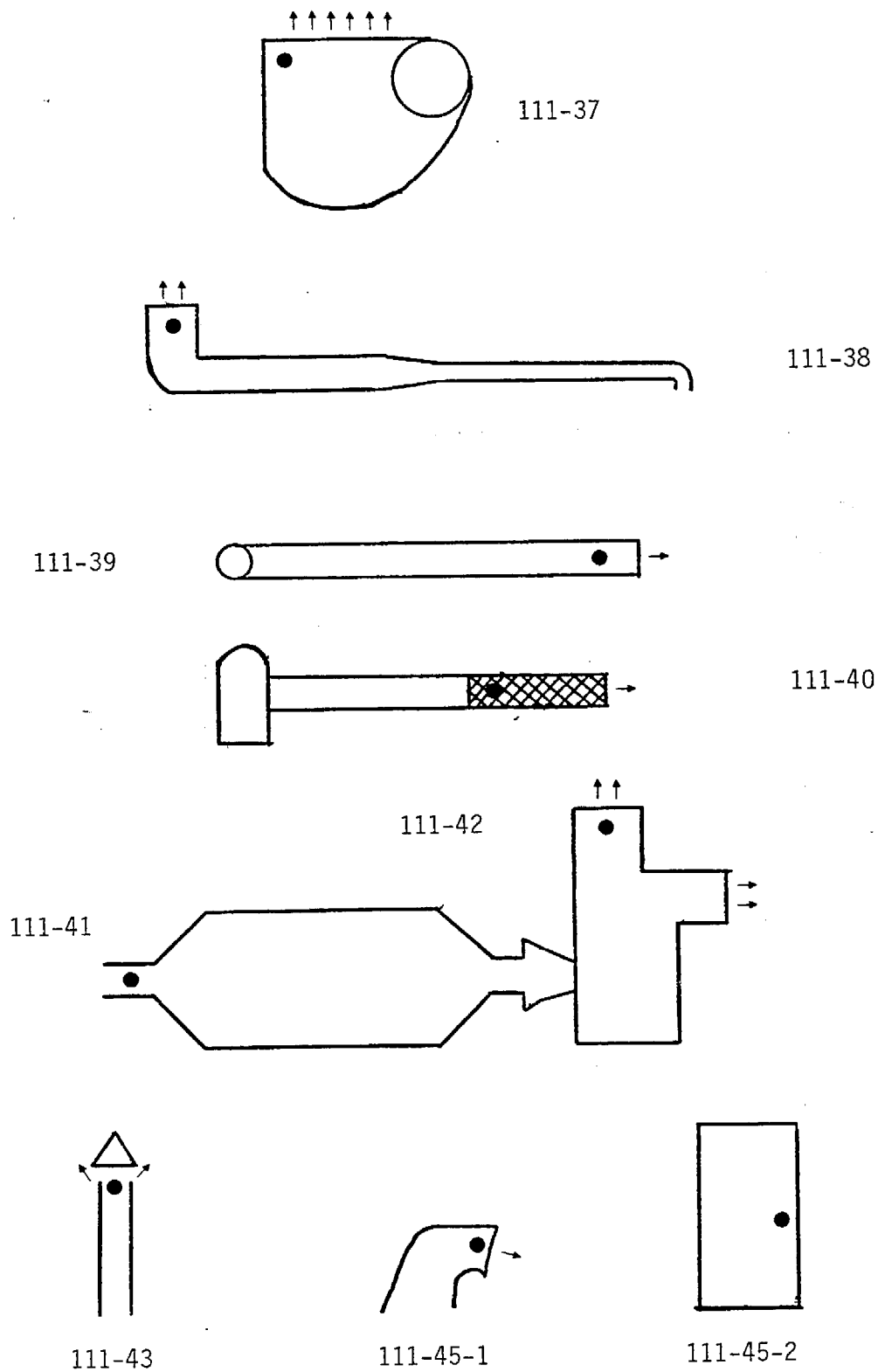


Figure 5.2-2. Configurations of Exhaust Vents and Ducts at Facility A

rounds--two on the afternoon of 18 March and two on the morning of 19 March--a second type of resin, containing 35 percent styrene and 5 percent MMA, was used in production. After the five rounds of forced-air emission sampling, we collected samples from the roof vent (Point 111-45-1) and the rear door (Point 111-45-2). Frequent checks were made with the plant management to assure that production was continuous throughout our testing.

Additional "sniff" tests were made at each point to determine whether pollutant concentrations were likely to vary significantly across the duct or outlet diameter. The only exhaust point at which more than a few percent variation was observed was Point 111-38, for which the minimum and maximum OVA readings were 40 and 55 ppm, respectively. It should be noted, however, that mass flow appeared to be nonsteady; i.e. the OVA readings at any given point in the cross-section varies by several ppm with time. In addition, as is discussed below, OVA readings at this exhaust point were probably influenced heavily by the presence of species other than styrene. We therefore assumed that the styrene concentration of the air drawn into our sampling device was typical of the actual exhaust concentration.

Two types of probes were used for sample collection. For Points 111-39 and 111-42, where the exhaust was quite hot, the probe was a 2.4-m (8-ft) copper tube. In all other cases, we used a 43-cm (17-in) stainless steel, ell-shaped tube. Both probes have a 0.32-cm (0.125-in) inside diameter. After the sampling, it was verified that the sampling flow rate was not diminished by the use of either probe. At Points 111-39 and 111-41, where a sampling port was available, the probe was inserted to roughly half the duct diameter. OVA sampling and collection of styrene on charcoal traps followed the procedures described in Appendix B.

Results and Discussion

Table 5.2-2 shows the results of our analyses of the charcoal trap samples collected at Facility A. Given the uncertainty in every aspect of sampling and analysis, concentrations are expressed as ranges. The low value results from assumption of a 1.0-L/min sampler flow rate and a styrene recovery factor of 0.9, while the high value results from use of 0.86 L/min and 0.8 for the two parameters, respectively. It is clear that the highest styrene concentrations are found in air vented from the impregnation table and the portions of the ovens where curing is not fully underway. It is for this

Table 5.2-2

STYRENE CONCENTRATIONS^a IN EXHAUST AIR AT FACILITY A

Sample ID No.	Emission Source	Styrene Concentration (µg/L)		Styrene Concentration (ppmv) ^b	
		Low	High	Low	High
111-37-1	Crosscut saw	6.2	8.1	1.5	1.9
111-37-4	Crosscut saw	4.6	6.0	1.1	1.4
111-37-5	Crosscut saw	14	18	3.2	4.2
111-38-1	Ovens	29	38	7.2	9.5
111-38-4	Ovens	110	140	27	36
111-39-1	Ovens	10	14	2.9	3.7
111-39-4	Ovens	13	17	3.5	4.6
111-40-1	Impregnation table	130	160	30	39
111-40-4	Impregnation table	330	430	78	100
111-41-1	Pre-Incinerator	2050	2700	500	660
111-41-5	Pre-Incinerator	3300	4300	780	1000
111-41-6	Pre-Incinerator	3600	4700	860	1100
111-42-1	Post-Incinerator	17	22	11	14
111-42-2	Post-Incinerator	19	25	12	16
111-42-4	Post-Incinerator	29	38	19	25
111-42-5	Post-Incinerator	19	25	13	16
111-43-1	ESP	8.0	11	1.9	2.5
111-43-4	ESP	37	48	8.5	11
111-45-1	Open roof vent	380	500	89	120
111-45-2	Rear doorway	250	330	58	77

^a Low: Sampler flow rate = 1.0 L/min, Recovery fraction = 0.9.^b High: Sampler flow rate = 0.86 L/min, Recovery fraction = 0.8. Adjusted for exhaust air temperature

reason that emissions from the impregnation table are directed to the rooftop incinerator.

On order to estimate mass flows of styrene from the facility, it is necessary to take air flow rates into account. Flow rates for all the exhaust points were obtained from the facility's engineering staff. While it would have been feasible to make our own flow measurements, we believed that the day-to-day variability of air flows would be considerably greater than the uncertainty in any measurements we could make. We therefore relied upon data provided by the facility's engineering staff, which had measured flows at several points within the last year.

Table 5.2-3 shows the mass flow rate of styrene from each forced-air exhaust point. Since emissions from Points 111-45-1 and 111-45-2 were principally by convection, it was not possible to estimate their magnitudes without considerably more information. That the styrene concentrations at these last two points were relatively high does not necessarily mean that emissions therefrom were high; indeed, given the ventilation system, the flow through the rear door (Point 111-45-2) could be expected to be inward at least part of the time. Additional comment is necessary in the case of Point 111-42, the afterburner outlet. Immediately downstream from the combustion chamber, dilution air is added by means of a venturi. We collected samples downstream from the dilution point, so that while styrene concentrations were half what they were upstream, the air flow rate was double. Therefore, the mass flow rate of pollutant was the same both upstream and downstream of the venturi.

The afterburner efficiency may be estimated from the data shown in Table 5.2-3. According to our results, the device removed from 98.4 to 98.8 percent of the incoming styrene mass.

Derivation of Emission Factors

For each charcoal trap sampling run, the starting and ending clock times were noted so that measured concentrations could later be associated with resin use rates. After all the sampling was completed, we obtained copies of the schedule by which resin was added to the production line. From this schedule we were able to compute, for any sampling interval, the average resin use rate, and hence the styrene input rate. As seen in Table 5.2-3, the

Table 5.2-3

ESTIMATE OF PROCESS EMISSION FACTORS FOR FACILITY A

Sample ID No.	Est. Styrene Emission		Resin Use (lb/min)	Styrene Flow (lb/min)	Emission factor (as Pct.)	
	Low (lb/min)	High (lb/min)			Low	High
111-37-1	0.0031	0.0040	24.0	9.6	0.032	0.042
111-37-4	0.0023	0.0030	9.6	3.4	0.068	0.088
111-37-5	0.0068	0.0089	20.2	7.1	0.096	0.13
111-38-1	0.0055	0.0072	30	12	0.046	0.060
111-38-4	0.020	0.027	12.5	4.4	0.45	0.61
111-39-1	0.00078	0.0010	12.7	5.1	0.015	0.020
111-39-4	0.00095	0.0013	23.8	8.3	0.011	0.016
111-40-1	0.037	0.049	12.7	5.1	0.73	0.96
111-40-4	0.099	0.13	20.0	7.0	1.4	1.9
111-41-1	0.26	0.34	12.7	5.1	5.1	6.7
111-41-5	0.41	0.54	20.0	7.0	5.9	7.7
111-41-6	0.45	0.59	16.1	5.7	7.9	10
111-42-1	0.0041	0.0054	12.7	5.1	0.080	0.11
111-42-2	0.0047	0.0062	20.8	7.3	0.064	0.085
111-42-4	0.0072	0.0095	21.7	7.6	0.095	0.13
111-42-5	0.0048	0.0063	22.7	8.0	0.060	0.079
111-43-1	0.00060	0.00079	12.7	5.1	0.012	0.015
111-43-4	0.0028	0.0036	21.7	7.6	0.037	0.047

flow of styrene through the system varied from 3.4 to 12 lb/min during our testing. The last two columns of Table 5.2-3 show the low and high ends, respectively, of our estimated confidence interval for the emission factor. As in the rest of this report, the emission factor is defined as the ratio of styrene emitted to styrene input to the system.

Emission factors for each major in-plant source are summarized in Table 5.2-4. The total uncontrolled emission factor was computed by including the afterburner intake but excluding the afterburner exhaust; i.e. by assuming that the afterburner did not exist. The total controlled emission factor includes the afterburner exhaust but not the input. It is seen that, while the afterburner is highly efficient in removing styrene from the impregnation table exhaust air, enough uncontrolled sources remain to result in an emission factor of 0.9 to 2.8 percent.

A review of all of the concentration, mass emission and emission factor data presented in this section shows an unexpected pattern: styrene emissions are generally higher when Resin 2 (35 percent styrene, 5 percent MMA) is used than when Resin 1 (40 percent styrene) is the main ingredient of the panels.

In summary, two emission factors will be used in estimating styrene emissions from continuous lamination plants. Where controls are absent, the emission factor will vary from 0.059 to 0.13. Where an afterburner is used, the emission factor will be 0.0092 to 0.028.

5.2.2 Source Tests at Facility B

Facility B is a medium-sized (120,000 lb resin per year) tank manufacturing plant in San Diego County. A preliminary site visit was made in March 1981. Emissions measurements were made on the afternoons of 31 March and 15 April 1981. Both days were sunny and clear, with afternoon temperatures around 29°C (75°F). Our initial conversations with plant management led us to believe that exhaust air flow data were available. As this proved not to be the case, we returned to the facility on 13 November 1981 to perform velocity traverses on the exhaust stack.

Facility and Process Description

The chief activity at this plant is the spray application of glass-reinforced polyester resin coating to 38- to 45-m³ (10,000- to 12,000-gal)

Table 5.2-4

SUMMARY OF ESTIMATED EMISSION FACTORS FOR PLANT A

(EF = 100 x mass styrene out/mass styrene throughput)

In-Plant Source	Resin 1 (40 Pct. Styrene)		Resin 2 (35 Pct. Styrene, 5 Pct. MMA)	
	Mean	Range	Mean	Range
Crosscut saw	0.037	0.037 - 0.042	0.096	0.068 - 0.13
Ovens (early in cure)	0.053	0.046 - 0.060	0.53	0.45 - 0.61
Ovens (late in cure)	0.018	0.015 - 0.020	0.014	0.011 - 0.016
Glass chopper	0.85	0.73 - 0.96	1.7	1.4 - 1.9
Impregnation table	5.9	5.1 - 6.7	7.9	1.4 - 1.9
Afterburner exhaust	0.095	0.08 - 0.11	0.086	0.060 - 0.13
Electrostatic precipitator	0.014	0.012 - 0.015	0.042	0.037 - 0.047
Total (Uncontrolled)	6.9	5.9 - 7.8	10	7.1 - 13
Total (Controlled)	1.1	0.92 - 1.2	2.5	2.0 - 2.8

steel tanks. All coating operations are conducted in a 4.6 x 12.2 x 4.6 m (15 ft x 40 ft x 15 ft) steel shed, a diagram of which is shown in Figure 5.2-3. At the start of the process, the tanks are sandblasted outdoors. Spray operations are conducted only during conditions of low or moderate humidity; during the season in which we made our tests, spraying generally began after 10 a.m.

One tank is sprayed at a time in the shed. The tank is carried into the shed on a low cart equipped with rollers and is moved to the approximate position shown in Figure 5.2-3. The entry door, which is at the opposite end of the shed from the exhaust stack, is left open, while the exit door remains closed during the spraying. One quarter of the tank's surface is coated at a time. Each coating cycle consists of three steps. First, the operator walks from the open end of the shed toward the closed end, applying a coat of resin with a spraygun attached to a travel arm. After this precoat is applied to the length of the tank, the operator returns to the starting point and then applies a coat of mixed resin and glass roving to the same quarter surface. These two passes take about 45 minutes. Finally, the tank is rotated 90 degrees and the cycle is repeated. The spraygun is thus operating for 180 minutes per tank. The actual manufacturing time is somewhat longer, since the first quarter coat must be substantially cured before coming into contact with the rollers for the application of the fourth quarter coating. This pause in spraying lasts about 20 minutes.

Emission Control and Exhaust Points

Makeup air enters the shed through the open door at one end. During spray operations (and only then), a 5-hp, 1735-rpm, 8-blade exhaust fan draws air through ducts located on the ceiling on either side of the closed end of the shed. The cylindrical exhaust stack is 91 cm (36 in) in diameter and extends 46 cm (18 in) above the roof line. No emission controls are installed.

Sampling Procedure

As will be described below, our sampling procedure differed between the two test days. In each case, however, air samples were drawn through a train consisting of 94 cm (20 ft) of 0.32-cm (0.125-in) inside diameter copper tubing, a cotton plug to remove fiberglass, and a charcoal trap. The cotton plug was replaced every half hour to avoid reduction of flow. The OVA pump

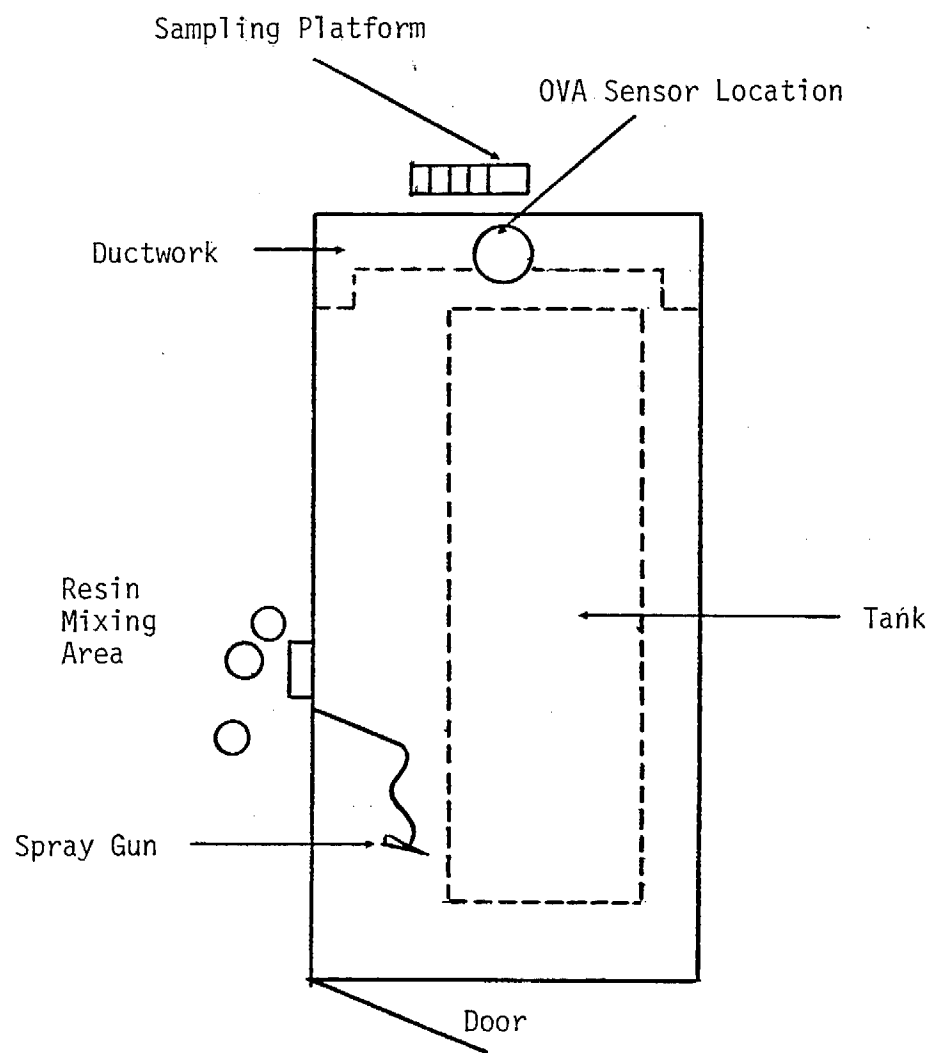


Figure 5.2-3. Plant Layout at Facility B (Scale: 1" = 10').

provided the suction for the sample collection. The copper tube inlet was placed approximately 20 cm (8 in) from the lip of the exhaust stack. The calibrated sampling flow rate was 1.0 L/min on the first day and 0.9 L/min on the second day.

On the day before each test, the OVA was calibrated by the procedures described in Appendix B. On each test day one or two charcoal traps were spiked in the field with known amounts of styrene and immediately sealed. As an additional quality control measure, blank traps were opened and immediately sealed in the field.

To measure exhaust velocity, a Kurz Model 415M hot-wire anemometer and an Ota Keiki Model 29-DGDC digital air velocity meter were placed at 16 points along two perpendicular diameters of the fanstack. Because the air flow was quite turbulent, velocity readings fluctuated considerably. We therefore maintained the sensor at one position for at least three minutes and noted a range of velocities in which about 90 percent of the readings fell. Readings were accurate to 0.05 m/s. Exhaust air velocity and volumetric flow rate were determined with values obtained by averaging six readings (three with the anemometer and three with the digital air velocity meter) at each measurement position. Readings with the air velocity meter were, on the average, 0.60 m/s higher than those on the anemometer; however, this difference was not significant at the 0.05 level ($t = 0.7584$, d.f. = 70).

Results and Discussion

First Day's Sampling. The purpose of the first day's sampling efforts was to obtain estimates of the ranges of styrene concentrations likely to be found in the plant exhaust during different portions of the production cycle. We thus kept a detailed log of activities in the spraying shed, so that they could be correlated with instantaneous OVA readings and concentrations determined from two- to five-minute integrated charcoal trap samples. The mean measured exhaust air velocity and flow rate were 3.2 m/s and 1.5 m³/s, respectively.

Table 5.2-5 presents the results of our GC analyses of the integrated charcoal trap samples. Analysis of Sample 111-48-1, which was spiked with 4530 ng of styrene in the field, indicated that 80.0 percent of the styrene present was recovered by our measurement technique. (Values reported in Table

Table 5.2-5

RESULTS OF GC ANALYSIS OF EXHAUST AIR GRAB SAMPLES
TAKEN AT FACILITY B, FIRST VISIT

Sample ID No.	Sampling Time (min)	Plant Activity During Sampling	Styrene Concentration	
			mg/m ³	ppm
111-48-2	5	Spraying of resin only	1105	259
111-48-3	3	Pause after resin spraying	441	103
111-48-4	5	Resin/glass spraying	1383	324
111-48-5	2	Resin/glass spraying, rollout ^a	879	206
111-48-6	5	Intermittent resin spraying at far end	1134	265
111-48-7	2.5	Resin spraying at near end	1730	405
111-48-8	2	No spraying; one door open ^b	410	96
111-48-9	3	Resin spraying (far end)	793	186
111-48-10	3	Resin spraying (near end)	1165	273
111-48-11	3	No spraying; both doors open	351	82

^a Spraying for 30 seconds; rollout for 30 seconds, spraying for 60 seconds.

^b Sample taken at open door, at opposite end of shed from the principal sampling point.

5.2-5 are for concentrations adjusted by a factor of 1.25). Concentrations in ppm by volume were calculated under the assumption that the exhaust air stream was at the measured ambient air temperature, 24°C.

Figure 5.2-4 shows instantaneous styrene concentrations as measured by the OVA during the test period. Readings made during consecutive one-minute intervals are joined by solid lines. In contrast to the situation at Facility A, where a continuous lamination process is used, styrene levels in the plant exhaust fluctuate considerably. Even the integrated samples taken on charcoal show that concentrations may vary by a factor of four during the spraying of one tank. It was therefore necessary to develop a sampling method which could provide an estimate of the integrated average styrene concentration in the exhaust air over a typical spraying cycle.

Fortunately, as seen in Figure 5.2-5, the correlation between the results of simultaneous OVA and charcoal trap sampling in the field was fairly high ($r = 0.78$). For the second visit, we attached a strip chart recorder to the OVA and devised a method of relating the height of the chart trace to the "true" styrene concentration measured by charcoal trap sampling. By field-calibrating the OVA in this way, we could then calculate integrated average styrene concentrations by planimetry. The method is described in detail in Appendix B.

Second Day's Sampling. Plant operations at Facility B on the second test day were identical to those on the first day, except that a different brand of polyester resin was used. According to the manufacturer, the resin on the second day had a specific gravity of 1.07 to 1.09 and contained 47 ± 2 percent styrene by weight. At approximately 1300 hours, the OVA sampler inlet was placed in the exhaust stack and the chart recorder began recording instantaneous organic vapor concentrations. Spraying operations began at 1336 hours and ended at 1451 hours. The chart recorder was turned off at 1453 hours.

Figure 5.2-6 shows portions of the chart recorder trace corresponding to the first 57 minutes of plant operations. The sudden drops in recorded organic vapor concentrations occurred each time that a charcoal trap was placed in series with the OVA; all styrene was presumably adsorbed onto the trap before it could reach the OVA's FID. Charcoal traps 111-53-1 and 111-53-2 were field-spiked with known amounts of styrene, as mentioned above.

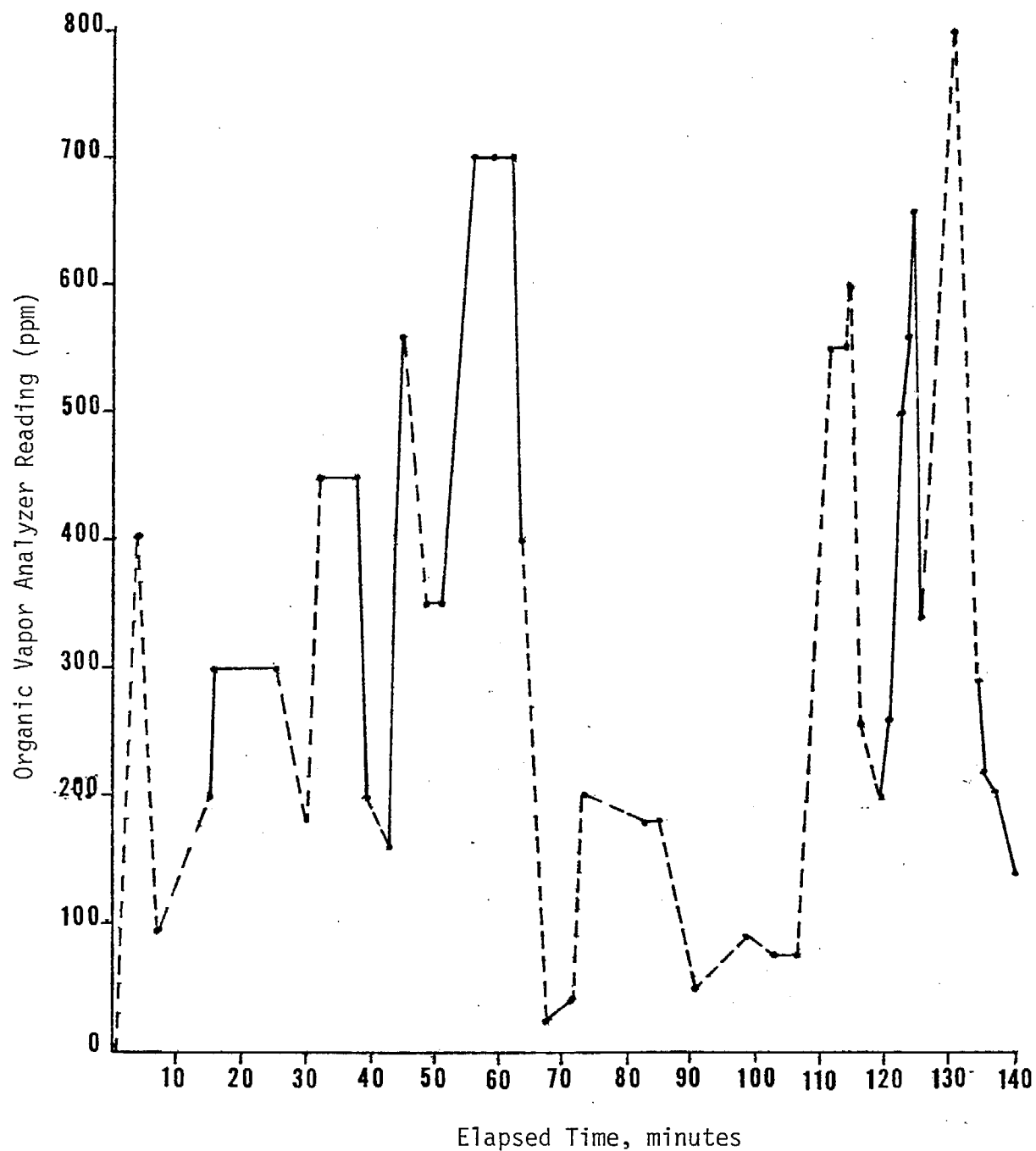


Figure 5.2-4. Instantaneous Exhaust Styrene Concentrations as Measured by Organic Vapor Analyzer at Facility B, First Visit. Solid Lines Connect Readings Made in Consecutive One-Minute Intervals

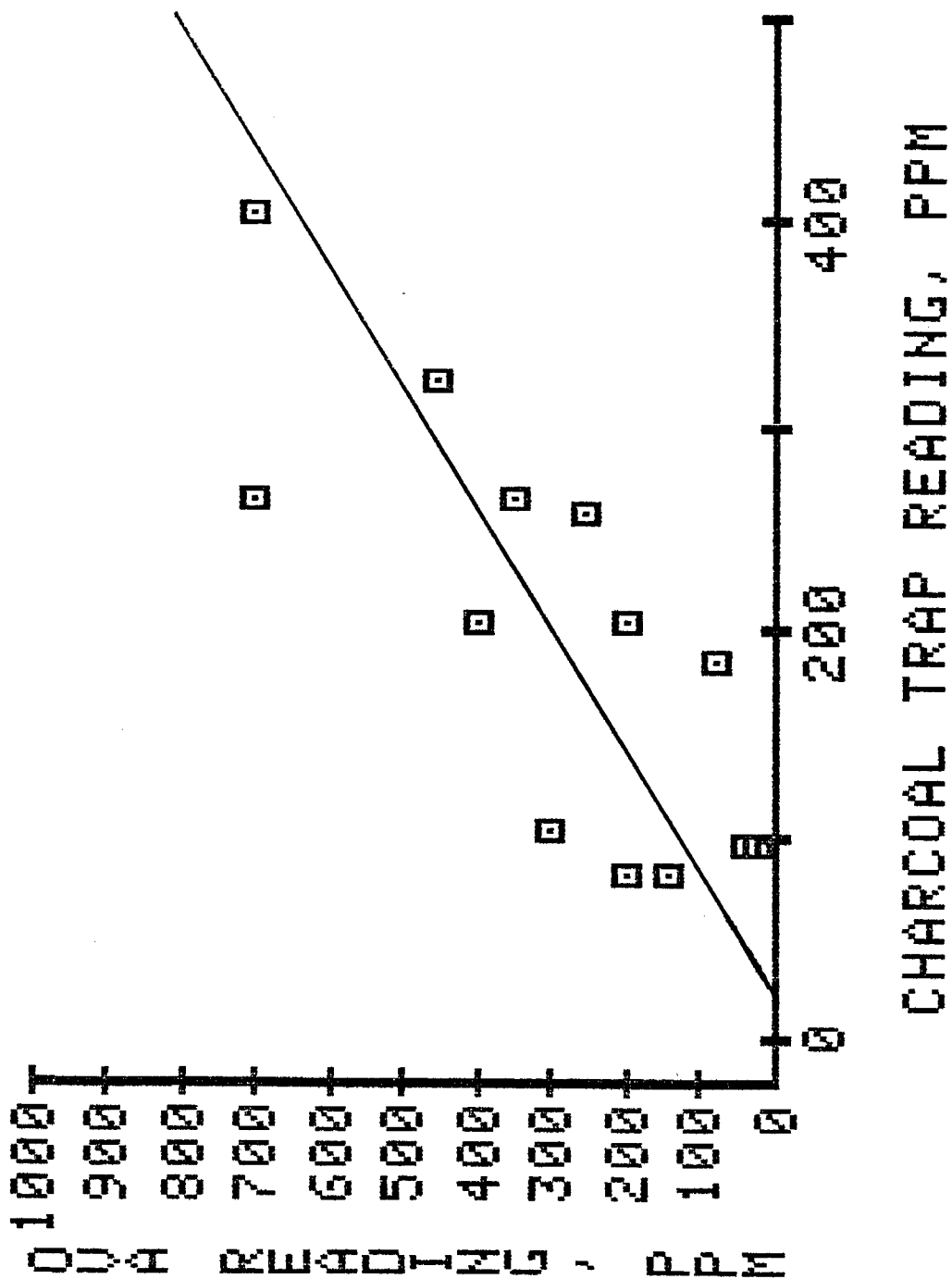


Figure 5.2-5. Organic Vapor Analyzer Readings vs. Charcoal Trap Sampling Results at Facility B, First Visit. Equation of the Regression Line is $OVA = 1.69 (TRAP) - 40.0$.

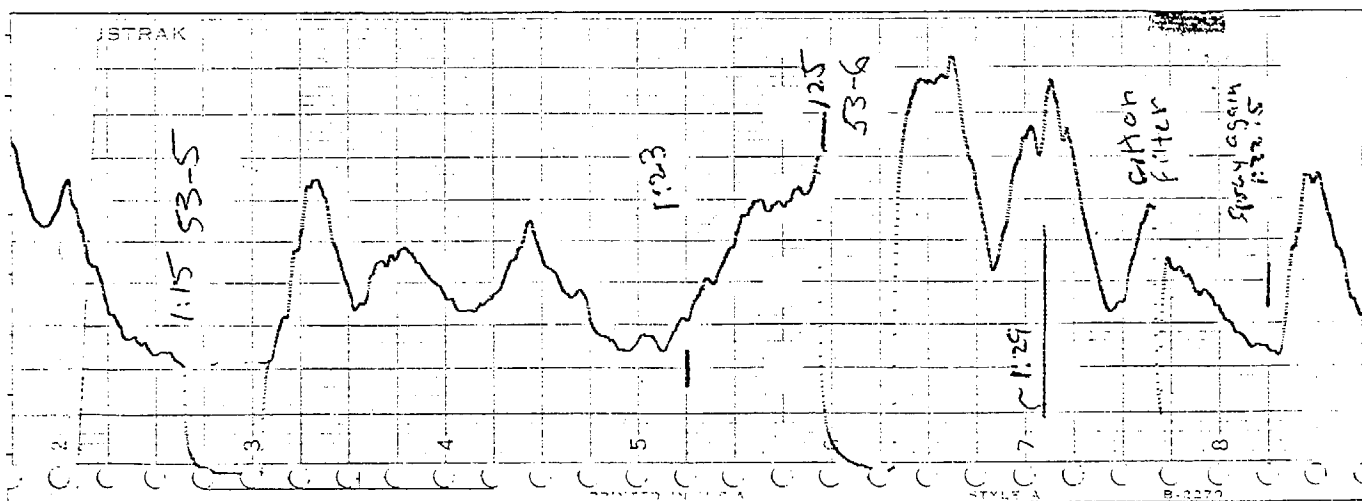
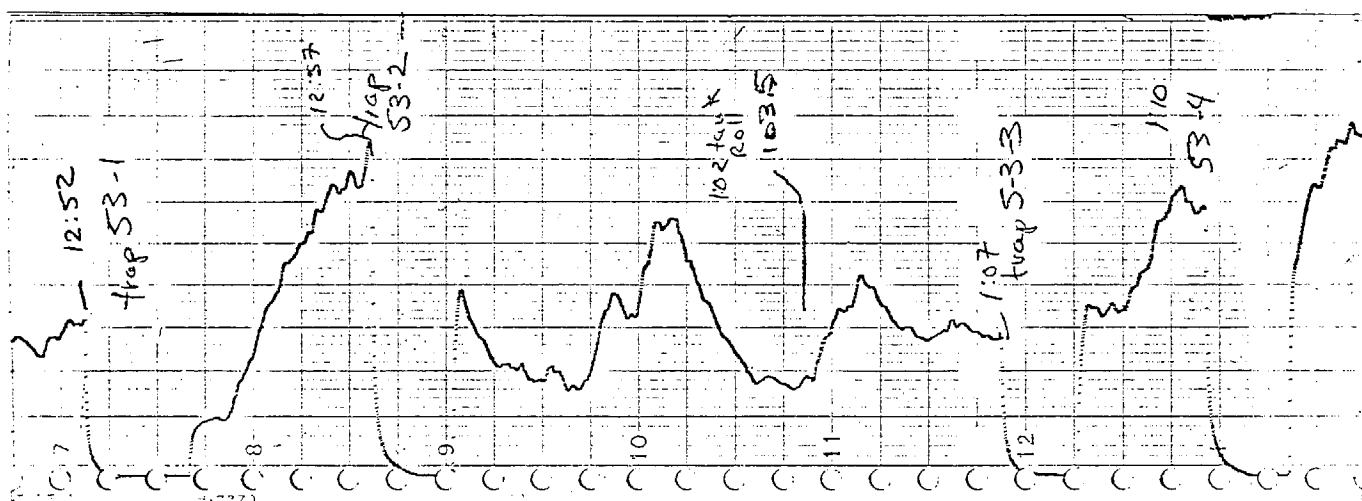
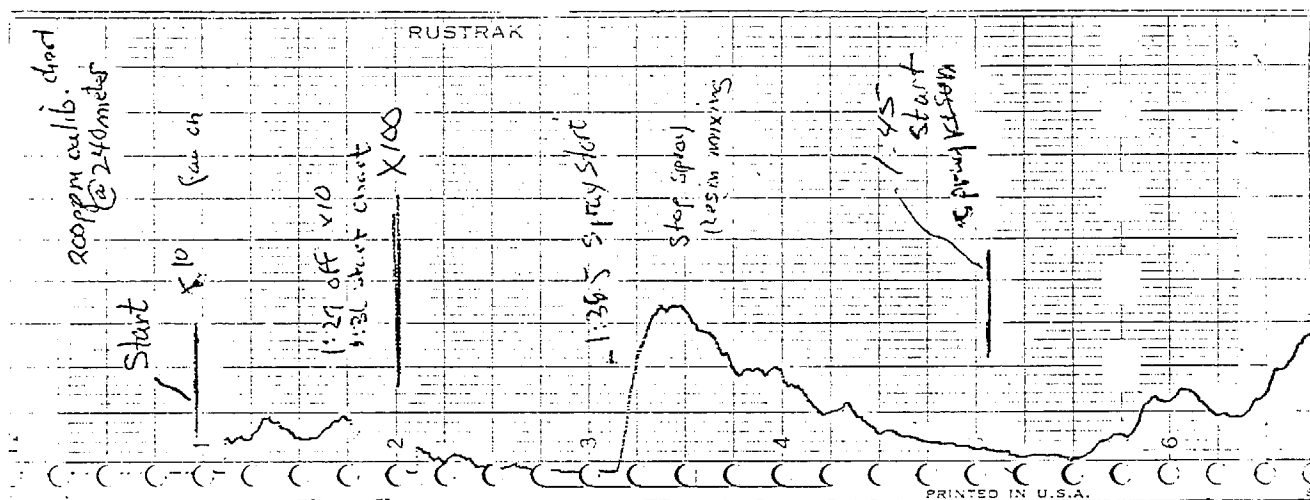


Figure 5.2-6. Recorder Trace of Instantaneous OVA Readings at Facility B, Second Visit

Traps 111-53-3 through 111-53-6 were used for calibrating the OVA trace. (Two additional calibration samples, not shown in Figure 5.2-6, were taken.) The shaded areas were measured by planimetry so that trap readings and integrated chart readings could be compared.

Table 5.2-6 shows, for each sample, the mass of styrene collected on the charcoal trap and the measured area under the recorder trace for the one-minute interval during which the trap sampling was conducted. Ideally, the ratio between chart area and mass collected should be the same for each sample. That it is not is due to variability in planimetry, in styrene recovery efficiency and instrument error. We have attempted to set rough bounds for this variability by adjusting the styrene mass/chart area ratio by the two recovery factors (0.82 and 0.86) determined from the spiked samples. The mean ratio was 63 g styrene per unit chart area, and the 95-percent confidence band for the mean was 55 to 71 g/unit area. Thus the maximum likely error for this calculation would be about 12 percent.

The area under that portion of the OVA trace corresponding to 145 minutes of plant operations, as measured by planimetry, was 2157 chart area units. Therefore by our method, the 95-percent confidence band for the amount of styrene emitted during that time interval would be 55×2157 to 71×2157 g. Given our sampling rate of 0.9 L/min and the 145-minute sampling time, the concentration of styrene in the plant exhaust was estimated to be 909 to 1174 g/L. As noted above, the measured exhaust air flow rate was $1.5 \text{ m}^3/\text{s}$. Mass emission rates were therefore determined to be the following:

	Emission Rate	
	<u>g/s</u>	<u>lb/hr</u>
Low Estimate	1.4	11
High Estimate	1.8	14

Derivation of Emission Factors

According to the plant operator, 263 kg (580 lb) of polyester resin was used during the test period. Since the styrene content of the resin was between 45 and 49 percent, between 118.4 and 128.9 kg of styrene entered the system. Low and high estimates of emission factors were calculated as follows:

Table 5.2-6
CALIBRATION OF OVA CHART RECORDER AT FACILITY B, SECOND VISIT

Charcoal Trap No.	Styrene Measured on Charcoal Trap (μg) ^a	OVA Chart Area ^b	μg Styrene per Unit of Chart Area Low ^c	High ^d
111-53-3	630.4	17.0	47.9	50.2
111-53-4	1378.5	27.3	65.2	68.4
111-53-5	508.8	12.0	54.8	57.5
111-53-6	1529.2	38.8	50.9	53.4
111-53-10	267	5.0	69.0	72.4
111-53-11	237	3.8	80.6	84.5

^a Uncorrected

^b Average of three or four planimetric measurements

^c Based on recovery factor of 0.86 and flow rate of 0.9 L/min

^d Based on recovery factor of 0.82 and flow rate of 0.9 L/min

$$\text{Low estimate} = \frac{\text{Minimum emission rate}}{\text{Maximum styrene input rate}}$$

$$\text{High estimate} = \frac{\text{Maximum emission rate}}{\text{Minimum styrene input rate}}$$

These quantities are:

$$\begin{aligned} (\text{EF})_{\text{low}} &= \frac{(909 \times 10^{-6} \text{ g/L}) (1.5 \text{ m}^3/\text{s}) (10^3 \text{ L/m}^3) (145 \text{ min}) (60 \text{ s/min})}{(128.9 \text{ kg})(1000 \text{ g/kg})} \\ &= 0.092 \end{aligned}$$

$$\begin{aligned} (\text{EF})_{\text{high}} &= \frac{(1174 \times 10^{-6} \text{ g/L}) (1.5 \text{ m}^3/\text{s}) (10^3 \text{ L/m}^3) (145 \text{ min}) (60 \text{ s/min})}{(118.4 \text{ kg})(1000 \text{ g/kg})} \\ &= 0.13 \end{aligned}$$

These emission factors are somewhat lower than those we derived in Section 5.1 from reports on previous tests of spraying operations (see Table 5.1-1). We believe, however, that our results are more credible, inasmuch as we took a 142-minute integrated sample rather than a few grab samples, and we measured the exhaust air flow, rather than depending upon fan ratings or other estimates. One very interesting finding is that if the emission factors calculated from our data are based upon resin use, rather than styrene mass input, then they bracket the emission factor used by the South Coast Air Quality Management District (SCAQMD) for this type of emission source; our low and high emission factors would be 0.041 and 0.064, respectively, compared to the SCAQMD emission factor of 0.05.

5.2.3 Source Tests at Facility C

Facility C is a fairly large (420,000 lb resin per year) synthetic marble plant in the South Coast Air Basin. A preliminary site visit was made on 17 June 1981, at which time it was arranged that the plant would use non-suppressed and vapor-suppressed resins on successive test days. Emissions measurements were made on 7 and 8 July 1981.

Facility and Process Description

All manufacturing activities at Facility C are conducted in a one-story rectangular building. Figure 5.2-7 is a schematic of the plant layout. On the two test days, the plant was manufacturing bathroom sinks of various sizes and shapes. The process begins on the west end of the building, where the casting resin is mixed with catalyst, fillers and colorants. Buckets of mixed resin are conveyed on an overhead trolley to the center of the plant. The resin is then hand-poured between the inner and outer shells of partially closed molds, which are conveyed by a belt to the east end of the plant. After a few minutes of curing, the outer shells of the molds are removed, and the sinks are placed in a drying oven. The inner shells are then removed, and the sinks are conveyed to a spray booth on the north side of the plant, where they are sprayed with gel coat. Finally, the gel-coated sinks are cured in an oven next to the spray booth.

Emission Control and Exhaust Points

A preliminary survey of the plant identified the following potential exhaust points for organic vapor emissions:

- Five fan vents along the east-west axis of the roof;
- Doors at either end of the building; and
- An exhaust vent connected to the spray booth and final curing oven

As is discussed below, organic vapor measurements were made at each potential emission point. No organic vapor emission control devices are used in this plant.

Sampling Procedure

On the first test day, the Foxboro Instruments Model OVA-128 organic vapor analyzer (OVA) described in previous sections was used to monitor styrene concentrations at the roof vents and the open doors. A Kurz Model 415M hot-wire anemometer was used to perform velocity traverses on the spray booth exhaust stack and the open doors.

On the afternoon of the first day and throughout the second day, emissions from the spray booth stack were measured by the same combination of charcoal trap sampling and OVA chart recording as was used for Facility B (see Section 5.2.2). On 7 July, the plant used a regular casting resin (i.e. with-

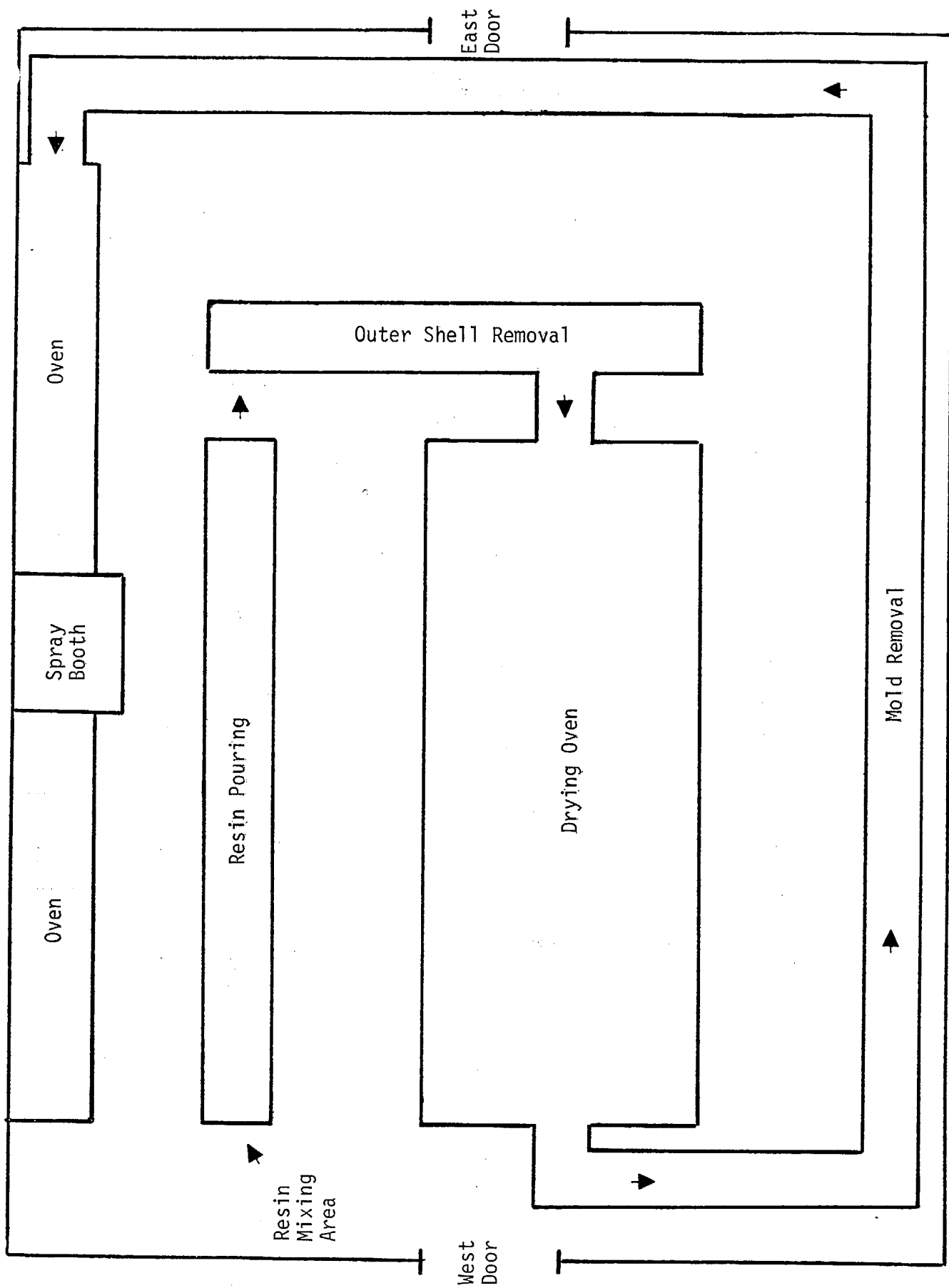


Figure 5.2-7. Plant Layout at Facility C (Not to Scale).

out vapor suppressant) having 37 percent styrene by weight. Continuous stack monitoring began at 1400 hours and ended at 1620 hours, for a total of 140 minutes. When we arrived at the plant on the morning of 8 July, the same resin was being used. The plant operators switched to a vapor-suppressed resin at 1030 hours, at which time we resumed our monitoring. The 173-minute monitoring period for the vapor-suppressed resin was 1037 to 1330 hours.

Results and Discussion

Roof vents: Styrene concentrations in the roof vent exhausts ranged from 5 to 9 ppm. Since these concentrations were far below those of the spray booth exhaust stack, and exhaust air flow was negligible, the roof vents were discounted as significant emission points.

End Doors: After our preliminary site inspection, we were concerned that an appreciable portion of the plant's organic vapor emissions could occur through the 4.3 x 3.7 m (14 x 12 ft) open doors at the ends of the building. These emissions would be quite difficult to monitor, given frequent changes in ambient wind speed and direction. We therefore divided the plane of each opening into quadrants and measured the wind speed and styrene concentration in each one. According to the OVA, the styrene concentration was essentially zero in all four quadrants of the west door and the lower half of the east door, and ranged from 1 to 2 ppm in the upper half of the west door. Spot measurements with the OVA confirmed that organic vapor concentrations were nearly zero inside the plant, near the doorways. Furthermore, we did not observe an appreciable flow of air from the major vapor-emitting processes (i.e. resin mixing, pouring, and gel coat spraying) towards the doors; instead, the main flow appeared to be toward the spray booth, which was equipped with an exhaust fan. Indeed, given the rather high spray booth exhaust air flow rate (see below), the net flow of air through the doors would have to be inward. We therefore discounted the doors as significant points of emissions to the outdoors.

Spray Booth Vent: The flow rate and mean velocity of the spray booth exhaust air were calculated to be $3.4 \text{ m}^3/\text{s}$ and 3.7 m/s , respectively. Figure 5.2-8 shows three typical sections of the recorder trace of the instantaneous OVA readings. Plant activities concurrent with the sampling are shown at the bottom of the trace. It is evident that styrene emissions are highest when gel coat is being sprayed in the booth. During times of no

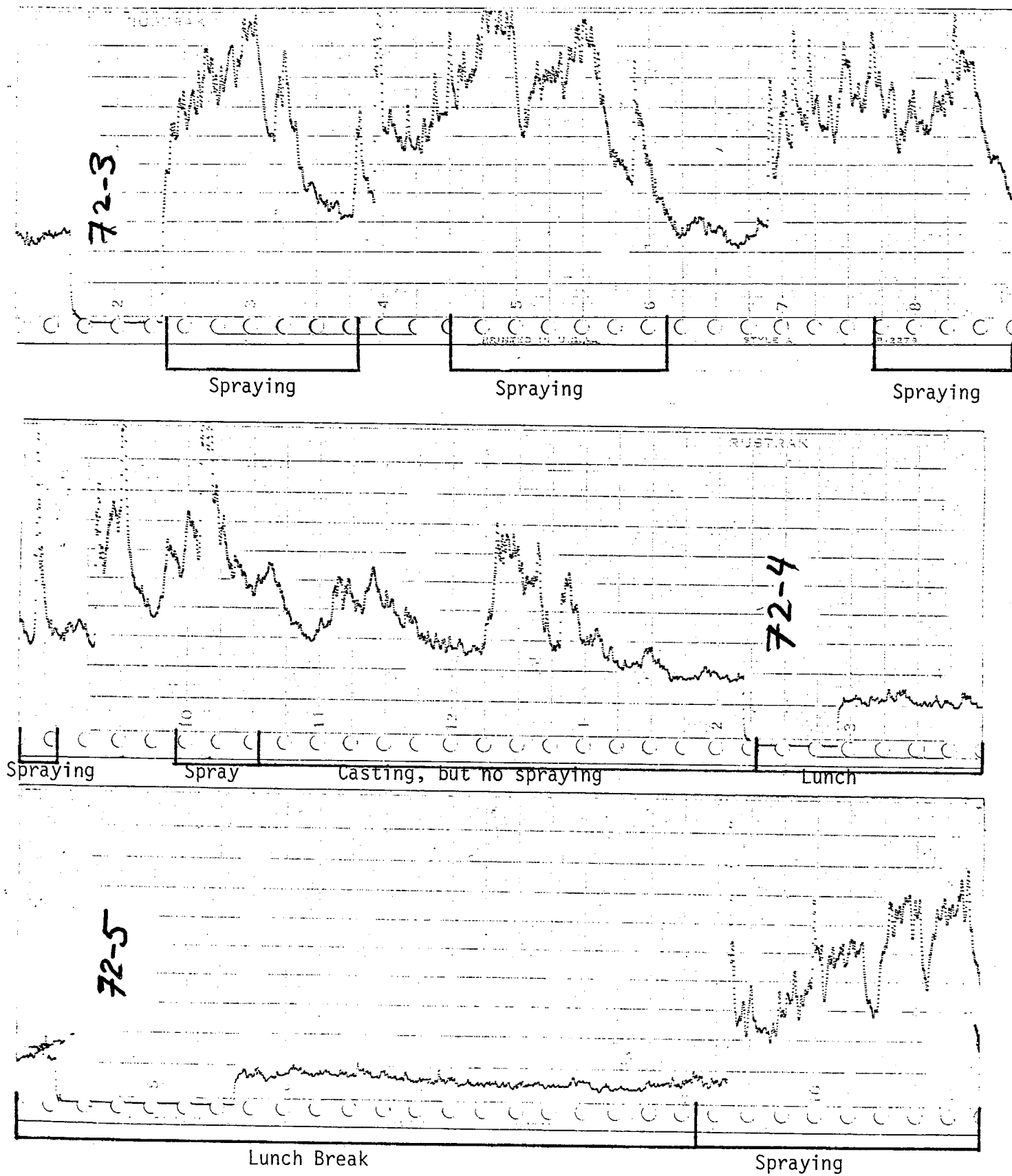


Figure 5.2-8. Recorder Trace of Instantaneous OVA Readings at Facility C, Second Day (Vapor-Suppressed Resin)

spraying, styrene concentrations in the exhaust decline but do not disappear; some of the styrene is probably carryover from the spraying, while some is due to emissions from casting. As seen in the second and third sections of the trace, the exhaust air styrene concentration began to drop at 1107 hours, when pre-lunch break spraying ended. For the next 12 minutes, casting operations continued, and styrene concentrations in the exhaust rose briefly and then began a gradual decline. During the lunch break, exhaust air styrene concentrations remained at about 5 to 10 ppm.

Table 5.2-7 shows the results of our GC analyses of charcoal trap samples and our planimetric measurements of corresponding OVA chart recorder traces. As was done for Facility B, minimum and maximum values for the ratio between styrene mass and chart area were calculated by using two recovery factors (0.80 and 0.81) determined from analysis of field-spiked samples, and two OVA sampling flow rates (0.95 and 0.97 L/min) determined from laboratory calibration. On 7 July, the mean value for the styrene mass/chart area ratio was 55.6 g/area unit, and the 95-percent confidence band was 5.1 to 6.2. On the following day, the ratio was (for an unknown reason) significantly smaller; the mean was 3.2 g/area unit and the 95-percent confidence band was 2.1 to 4.3.

Table 5.2-8 summarizes the calculation of emission rates from the stack monitoring data. It appears that the mass emission rate of styrene is slightly lower when the vapor-suppressed resin is used, although we hasten to note that there is so much overlap in the 95-percent confidence intervals about the means for the two resin types that the difference in means may not be statistically significant. In either case, however, the mass emission rate is lower than that observed for the general purpose polyester resin spraying operations conducted at Facility B.

Derivation of Emission Factors

Because styrene-laden air from the casting operations is commingled with air in the gel coat spray booth, it is impossible to derive separate emission factors for the two processes. The recorder traces from the spray booth exhaust monitoring make it clear that the bulk of the styrene emissions are due to the spraying. We have therefore estimated two types of emission factors: one for the overall operation, and one for gel coat spraying alone.

Table 5.2-7

CALIBRATION OF OVA CHART RECORDER AT FACILITY C

Charcoal Trap No.	Styrene Measured on Charcoal trap (μg) ^a	OVA Chart Area ^b	μg Styrene per Unit of Chart Area Low ^c	High ^d
<u>7 July 1981 Sampling</u>				
117-71-1	87.0	20.0	5.5	5.7
117-71-2	51.5	13.0	5.0	5.2
117-71-3	131.1	27.5	6.1	6.3
<u>8 July 1981 Sampling</u>				
117-72-1	95.5	31.7	3.8	4.0
117-72-4	14.2	9.1	2.0	2.1
117-72-6	42.4	28.0	1.9	2.0
117-72-11	114.6	30.0	4.9	5.0

^a Uncorrected.^b Average of two or three planimetric measurements.^c Based on recovery factor of 0.81 and flow rate of 0.97 L/min.^d Based on recovery factor of 0.80 and flow rate of 0.95 L/min.

Table 5.2-8
CALCULATION OF STYRENE EMISSIONS FROM FACILITY C

	Sampling Date	
	7 July	8 July
Resin type	Non-suppressed	Suppressed
Sampling time	140 min	173 min
OVA chart area	2131 units	3601 units
Styrene/chart area	5.1 - 6.2 $\mu\text{g}/\text{unit}$	2.1 - 4.3 $\mu\text{g}/\text{unit}$
Mass emission	10.9 - 13.2 mg	7.6 - 15.5 mg
Sampling volume ^a	140 L	173 L
Styrene conc. in exhaust	78 - 94 $\mu\text{g}/\text{L}$	44 - 90 $\mu\text{g}/\text{L}$
Exhaust air flow	3.4 m^3/s	3.4 m^3/s
Mass emission rate	0.27 - 0.32 g/s	0.15 - 0.31 g/s
Mass emission rate	2.2 - 2.6 lb/hr	1.2 - 2.6 lb/hr

^aCorrection for volume flow rate was made in calculating styrene/chart area ratio.

According to the plant operator, the normal production rate is 20 sinks per hour. During the 173-minute monitoring period on the second test day, we counted 60 sinks starting on the casting line. Assuming a steady flow of fixtures through the assembly line, the observed production rate was therefore 20.8 sinks per hour. Given the variability in production from day to day, we have assumed in the following calculations that the nominal 20 sink/hour rate was valid for both test days. On the first test day, the plant operator provided us with a tabulation of resin and gel coat use for the entire day's production. To make 47 sinks, 481 lb of casting resin and 42 lb of gel coat were used. The resin use rates were therefore 4.62 kg (10.2 lb) casting resin and 0.408 kg (0.9 lb) gel coat per sink. The casting resin and gel coat used at the plant contain 37 and 40 percent styrene by weight, respectively.

Table 5.2-9 summarizes the calculation of emission factors for this plant. From 1.4 to 3.1 percent of the styrene entering the plant as cross-linking agent in the casting resin and gel coat is emitted to the atmosphere. By basing the emission factor upon styrene input we can avoid the problem of distinguishing between casting resin and gel coat emissions. By assuming that all the emissions are due to gel coat spraying, however, we can set an upper bound for a gel coat emission factor. The styrene-based emission factor for the gel coat is estimated to be 0.30 to 0.35 for the first test day and 0.166 to 0.34 for the second test day; the absolute upper bound would thus be about 0.35. As has been mentioned several times before, various regulatory agencies have traditionally based the emission factor upon total gel coat use, rather than upon styrene. In our case, the upper bound for this "conventional" type of emission factor is estimated by multiplying the styrene-based factor by the fraction of styrene in the gel coat, 0.4. The result, 0.14, is higher than the value of 0.10 used by the South Coast Air Quality Management District. But then, at least some of the styrene emissions entering into the calculation were probably really due to casting resin use.

Finally, it is not possible to draw a firm conclusion about the effectiveness of vapor suppressants in reducing styrene emissions from this facility. The fact that the lower bound of the emission factor estimate is lower for the vapor-suppressed resin than for the conventional casting resin is probably due more to the greater variance in our measurements of the styrene/OVA chart area ratio than to a real difference in emissions. In addition, differences in casting resin styrene emissions could have been masked by emissions from the gel coat spraying.

Table 5.2-9
CALCULATION OF EMISSION FACTORS FOR FACILITY C

Casting Resin Type ^a	Styrene Emission Rate (g/s)	Test Period (min)	Styrene Emitted (kg)	Casting Resin Use (kg)	Gel Coat Use (kg)	Total Styrene Input (kg)	Emission Factor ^b	
NVS	0.27 - 0.32	140	2.3 - 2.7	216	19.0	87.5	Low	0.026
VS	0.15 - 0.31	173	1.6 - 3.2	267	23.5	108.2	High	0.031
							Low	0.014
							High	0.030

^a NVS = Non-vapor-suppressed resin, VS = vapor-suppressed resin.

^b Emission factor = Mass styrene out/mass styrene throughput.